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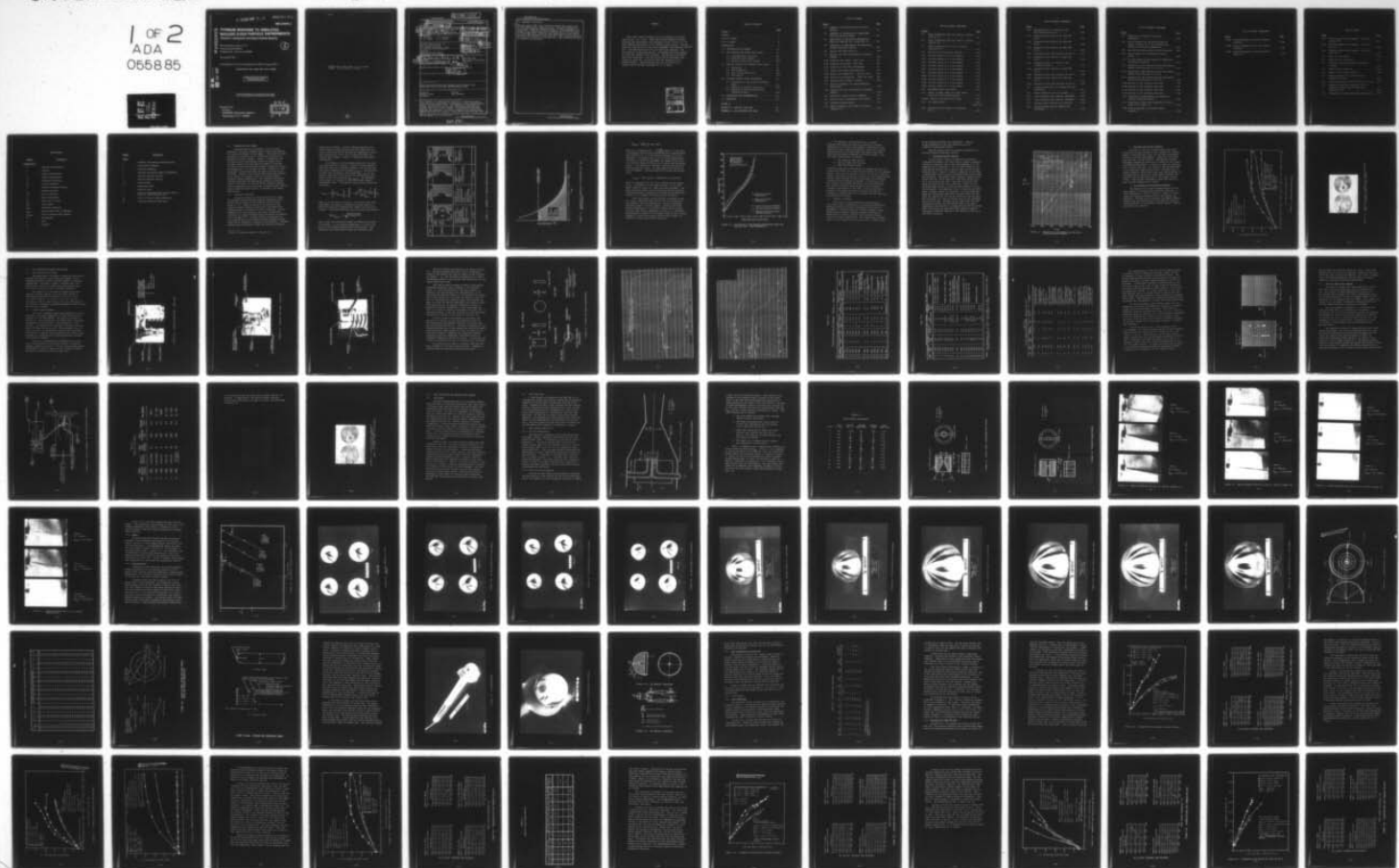
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# **TITANIUM RESPONSE TO SIMULATED NUCLEAR CLOUD PARTICLE ENVIRONMENTS**

**Volume I—Analytical and Experimental Results**

Science Applications, Inc.  
101 Continental Blvd.  
El Segundo, California 90245

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31 August 1977

Final Report for Period September 1976—August 1977

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20. ABSTRACT (Continued)

Erosion Tunnel (DET), and a particle impact test series using the SAI hypervelocity impact facility. Analytical modeling of titanium oxidation produced results in close agreement with experiment. Although increased oxidation of titanium was confirmed in  $H_2O$  vapor versus  $O_2$  environment tests, no net effect of liquid  $H_2O$  and  $O_2$  oxidation under combined particle erosion conditions was observed in the AEDC DET. This is believed to be the result of the heat of vaporization of  $H_2O$  exceeding the heat of oxidation of  $H_2O$  vapor.

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## PREFACE

This final report documents the work completed by Science Applications, Inc. (SAI), under DNA contract DNA001-76-C-0366. This work was sponsored by the Aerospace Systems Division of the Shock Physics Directorate of the Defense Nuclear Agency. The program was conducted during the period September 1976 through August 1977. The DNA technical monitor was Major Don Anderson. The SAI Principal Investigator was Mr. Lyle Dunbar who also directed the AEDC Dust Erosion Tunnel testing. The oxidation and impact tests were performed in the SAI Electro-optics and Impact Laboratory at Santa Ana, California under the direction of Mr. George Burghart. Analytical modeling was performed by Dr. Richard Clever and SAI consultant Dr. A. F. Mills.

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## TABLE OF CONTENTS

	<u>Page</u>
 VOLUME I:	
PREFACE . . . . .	1
LIST OF FIGURES . . . . .	3
LIST OF TABLES . . . . .	8
NOMENCLATURE . . . . .	9
1.0 INTRODUCTION AND SUMMARY . . . . .	1-1
2.0 SAI OXIDATION AND IMPACT TEST SERIES . . . . .	2-1
2.1 Test Objectives and Scope . . . . .	2-1
2.2 Oxidation Test Program . . . . .	2-1
2.3 Particle Impact Test Program . . . . .	2-14
3.0 AEDC DET EROSION AND OXIDATION TEST SERIES . .	3-1
3.1 Background . . . . .	3-1
3.2 Test Objectives . . . . .	3-2
3.3 Test Program Description . . . . .	3-2
3.4 Test Results . . . . .	3-32
4.0 TITANIUM RESPONSE MODEL DEVELOPMENT . . . . .	4-1
4.1 Formulation of the Titanium Oxidation Model . . . . .	4-1
4.2 Analysis of Oxidation Test Data . . . . .	4-35
4.3 Coupling of Particle Erosion and Oxidation Effects . . . . .	4-42
5.0 CONCLUSIONS AND RECOMMENDATIONS . . . . .	5-1
6.0 REFERENCES . . . . .	6-1
 VOLUME II:	
APPENDIX A: AEDC DET TEST DATA	A-1
APPENDIX B: SAI OXIDATION TEST DATA	B-1

## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1-1 Schematic of Titanium Surface Reaction Process. . . . .	1-3
1-2 Schematic of Constraints on Oxygen Mass Flux into Solid Titanium . . . . .	1-4
1-3 Application of the Heating Augmentation Model for AEDC DET Run 9 (from Ref. 4) . . .	1-6
1-4 Comparison of Experimental and Analytical Titanium Oxidation Results . . . . .	1-9
1-5 Results from AEDC DET Run 5. . . . .	1-11
1-6 Typical Post Test Photographs of Titanium Samples. . . . .	1-12
2-1a Oxidation Test Stand - Front View. . . . .	2-2
2-1b Oxidation Test Stand - Rear View . . . . .	2-3
2-1c Close-Up of Test Tube and Specimen . . . . .	2-4
2-2 Typical Test Model Configurations. . . . .	2-6
2-3a Typical Low Temperature - Long Run (#7). . .	2-7
2-3b Typical High Temperature - Short Run (#18) .	2-8
2-4 Oxidation Data Trends at 1500°K. . . . .	2-13
2-5 Facility Schematic for Impact/Oxidation Experiments. . . . .	2-15
2-6 Typical Post Test Photographs of Titanium Samples. . . . .	2-18
3-1 Water/Dust Injection Strut Schematic . . . .	3-3
3-2 Conical Inlet, Counterbored Exit Design. . .	3-6
3-3 Straight Through Design. . . . .	3-7
3-4 Water Calibration for 0.062 in. Orifice (Scenes 1-3) . . . . .	3-8

# LIST OF FIGURES (CONTINUED)

<u>Figure</u>		<u>Page</u>
3-5	Water Calibration Test for 0.040 in. Orifice (Scenes 4-6) . . . . .	3-9
3-6	Water Calibration Test for 0.020 in. Orifice (Scenes 7-9) . . . . .	3-10
3-7	Water Calibration for 0.02 in. Orifice (Scenes 10-12) . . . . .	3-11
3-8	Water Orifice Calibration Results. . . . .	3-13
3-9a	Pre-Test Photos of 2.0 Inch Models . . . . .	3-14
3-9b	Pre-Test Photos of 2.0 Inch Models . . . . .	3-15
3-9c	Pre-Test Photos of 2.0 Inch Models . . . . .	3-16
3-9d	Pre-Test Photos of 2.0 Inch Models . . . . .	3-17
3-9e	Pre-Test Photos of 2.0 Inch Models . . . . .	3-18
3-9f	Pre-Test Photos of 2.0 Inch Models . . . . .	3-19
3-10a	Pre-Test Photos of 3.0 Inch Models . . . . .	3-20
3-10b	Pre-Test Photos of 3.0 Inch Models . . . . .	3-21
3-10c	Pre-Test Photos of 3.0 Inch Models . . . . .	3-22
3-10d	Pre-Test Photos of 3.0 Inch Models . . . . .	3-23
3-11	Hemisphere Model Description . . . . .	3-24
3-12	Sketch of Model Holder for Those Models Using Spot Welded Thermocouples. . . . .	3-26
3-13a&b	Pressure and Temperature Probes. . . . .	3-27
3-14	Gas Sampler Model. . . . .	3-29 thru 3-31
3-15	Stagnation Point Results for AEDC DET Run 2. . . . .	3-36



# LIST OF FIGURES (CONTINUED)

<u>Figure</u>		<u>Page</u>
3-16	Stagnation Point (0 Degrees, TC #1) Heat Transfer for Run 2. . . . .	3-37
3-17	Stagnation Point Results for AEDC DET Run 3. . . . .	3-39
3-18	Stagnation Point Results for AEDC DET Run 4. . . . .	3-40
3-19	Stagnation Point Results for AEDC DET Run 5. . . . .	3-42
3-20	Stagnation Point Heat Transfer for Run 5 . .	3-43
3-21	Stagnation Point Results for AEDC DET Run 6. . . . .	3-46
3-22	Stagnation Point (5° Location) Heat Transfer for Run 6 . . . . .	3-47
3-23	Stagnation Point Results for AEDC DET Run 7. . . . .	3-49
3-24	Stagnation Point Heat Transfer for Run 7 . .	3-50
3-25	Stagnation Point Results for AEDC DET Run 8. . . . .	3-51
3-26	Stagnation Point Heat Transfer for Run 8 . .	3-52
4-1	Difusion Coefficient in Titanium from the Literature . . . . .	4-9
4-2	Phase Diagram for the Ti-O System. . . . .	4-11
4-3	Total Oxidation Rate Constant [STRINGER] . .	4-14
4-4	Total Oxidation Rate Constant [KOFSTAD]. . .	4-14
4-5	Oxidation Rate Constant for Ti-6Al-4v. . . .	4-17
4-6	Titanium Steam Reaction Löhberg and Schleicher . . . . .	4-19



# LIST OF FIGURES (CONTINUED)

<u>Figure</u>		<u>Page</u>
4-7	Comparison of Oxygen and Steam Gas Consumption. . . . .	4-20
4-8	Energy Produced per gm-atom of Reacting Oxygen (16 gm O) in Ti for Different End Products and Reaction Temperature. . . . .	4-22
4-9	Equilibrium Concentrations for Pure Titanium .	4-23
4-10	Phase Diagram for the Hydrogen-Titanium System . . . . .	4-24
4-11	Titanium Phases as They Depend on Temperature and Hydrogen Pressure. . . . .	4-24
4-12	Comparison of SAI Predictions and Experimental Results from Reference 10 (0.5°C/s). . . . .	4-31
4-13	Comparison of SAI Predictions and Experimental Results from Reference 10 (8°C/s). . . . .	4-32
4-14	Comparison of SAI Predictions and Experimental Results from Reference 10 (22°C/s) . . . . .	4-34
4-15a	Analysis of SAI Oxidation Data Runs. . . . .	4-36
4-15b	Analysis of SAI Oxidation Data Runs. . . . .	4-37
4-15c	Analysis of SAI Oxidation Data Runs. . . . .	4-38
4-15d	Analysis of SAI Oxidation Data Runs. . . . .	4-39
4-16	Comparison of Experimental and Analytical Titanium Oxidation Results . . . . .	4-40
4-17	Comparison of Model with Experiment for Run 7, Model TI-22, Clear Air . . . . .	4-41
4-18a	Titanium Response to Particle Impact-Oxidation. . . . .	4-46

LIST OF FIGURES (CONTINUED)

<u>Figure</u>		<u>Page</u>
4-18c	Titanium Response to Particle Impact- Oxidation. . . . .	4-48
4-18d	Titanium Response to Particle Impact- Oxidation. . . . .	4-49
4-18e	Titanium Response to Particle Impact- Oxidation. . . . .	4-50

# LIST OF TABLES

<u>Table</u>		<u>Page</u>
2-1a	Titanium Oxidation Run Summary: Series 1, January 1977 . . . . .	2-9
2-1b	Titanium Oxidation Run Summary: Series 2, May 1977 . . . . .	2-10
2-1c	Titanium Oxidation Run Summary: Series 3, July 1977. . . . .	2-11
2-2	Phase III Test Matrix. . . . .	2-16
3-1	Water Orifice Calibration. . . . .	3-5
3-2	Pre-Test Titanium Hemisphere Thicknesses (Inches) . . . . .	3-25
3-3	AEDC DET Test Conditions . . . . .	3-33
3-4	Results of Gas Sample Analysis . . . . .	3-44
4-1	Oxygen Pressures in Investigations of Unalloyed Titanium . . . . .	4-15
4-2	Equilibrium Compositions of Steam at 0.3 atm .	4-16
4-3	Summary of Specimens (Ti6Al-4V) Used to Compare Predicted Reaction Rate with Experiment (10). . . . .	4-30
4-4	Parameters for Impact-Oxidation Calculation. .	4-44

## NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>
<u>Alphabetical</u>	
A	reaction rate constant
B	constant
C	oxygen concentration
$C_s$	oxygen concentration
D	diffusion coefficient
$d_p$	particle diameter
E	reaction activation energy
$H_r$	recovery enthalpy
$\Delta H_s$	heat of reaction
K	oxygen consumption
$\dot{m}_{O_2}$	mass flux of oxygen
$M_{O_2}$	total oxygen
$Q_{cw}$	cold wall convection
$Q_{vap}$	rate at which heat is absorbed
$\dot{q}_{react}$	rate of chemical heat release
R	gas constant
t	time
V	velocity



<u>Symbol</u>	<u>Definition</u>
<u>Greek</u>	
$\gamma$	constant in parabolic oxidation model
$\epsilon$	oxide scale thickness
$\zeta$	titanium thickness
$\eta$	fraction of particle energy transferred
$\rho$	material specific gravity
$\rho_p$	particle specific gravity
$\rho_{cl}$	cloud density
$\tau$	obscuration time
$\chi$	material depth
$\alpha$	ratio of projected crater surface area to particle cross-sectional area
$\alpha_H$	depth of kinetic energy deposition
$\Delta W$	titanium oxidation weight gain

## 1.0 INTRODUCTION AND SUMMARY

Extensive testing and analyses (1-5)\* have been conducted to develop a response model (erosion and heating) for titanium subjected to dust impacts. This model has been successful in a broad range of ground test facilities in predicting titanium response. However, consideration has not been given to the combined effects of nuclear cloud ice/water particle and dust particle impacts on titanium. In general, dust particle impacts would be expected to be an over-simulation of ice impacts and thus, a design to a dust environment of equivalent mass concentration would be conservative. However, there remains some uncertainty relative to the effect of ice/water impacts on titanium surface chemistry heating augmentation. This document describes a combined analytical and experimental program to bound the effects of ice/water on titanium surface chemical reaction heating augmentation and to develop an improved heat transfer model to describe these effects, if necessary, for design applications.

### 1.1 Technical Background

Extensive studies of titanium oxidation have shown the dominant surface chemistry heating augmentation mechanism to be the result of the formation of solid state oxides (3, 4). Oxygen available at the surface of the titanium diffuses through a protective oxide coating and releases energy in the form of a heat of solution. As the temperature of the titanium or the oxygen concentration increases, the oxygen diffuses faster and energy is released at an increased rate. Titanium ignition occurs when the heat released due to the chemical reaction exceeds the heat losses due to convection, conduction, and radiation. Titanium nosetips must be designed to stay well below this ignition

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\* Refers to reference numbers in Section 6.0.

temperature threshold. Particle impacts complicate the oxidation/heat release process since they remove the protective oxide coating and increase the temperature locally, thus increasing the local rate of oxygen diffusion and chemical heat release. Figure 1-1 describes this process schematically.

Past studies (4) have produced models for the chemical heat release in titanium. Figure 1-2 shows schematically that the rate of oxygen diffusion into titanium (and thus rate of chemical heat release  $\dot{q}_{\text{react}}$ ) is controlled by the mass flux of oxygen at the surface  $(\dot{m}_{\text{O}_2})_{\text{gas}}$  (in the boundary layer flow field) and by the rate of oxygen diffusion in the solid titanium  $(\dot{m}_{\text{O}_2})_{\text{solid}}$ . The dominating rate process is a function of the time between impacts  $\tau$  (obscuration time). The chemical reaction heat release can be written:

$$\dot{q}_{\text{react}} = 2 \left[ (\dot{m}_{\text{O}_2})_{\text{solid}} \right]_{t=\tau} \left[ 1 - \left( \frac{1}{2} \right) \frac{\left[ (\dot{m}_{\text{O}_2})_{\text{solid}} \right]_{t=\tau}}{(\dot{m}_{\text{O}_2})_{\text{gas}}} \right] \Delta H_s$$

where  $\Delta H_s$  is the heat of solution. For typical dust cloud conditions, the process is dominated by solid phase diffusion (this must be reexamined for nuclear ice cloud conditions). The oxygen diffusion into the solid can be written:

$$(\dot{m}_{\text{O}_2})_{\text{solid}} = C_s \sqrt{\frac{A \exp(-E/RT)}{\pi t}}$$

where A and E are constants related to diffusion of oxygen in titanium, T is the titanium temperature, t is the time, and  $C_s$  is the oxygen concentration at the surface. Combining the above expressions yields the functional form



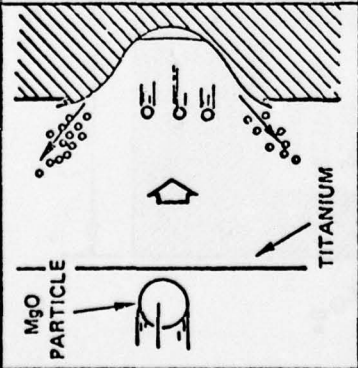
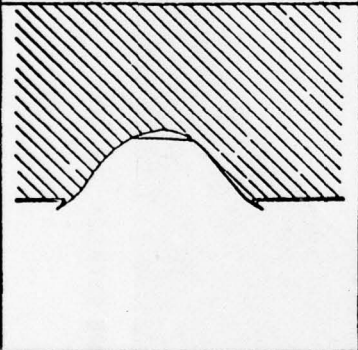
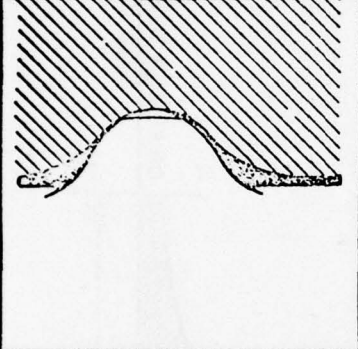
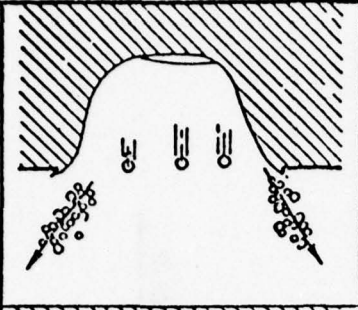
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FIGURE 1-1. SCHEMATIC OF TITANIUM SURFACE REACTION PROCESS



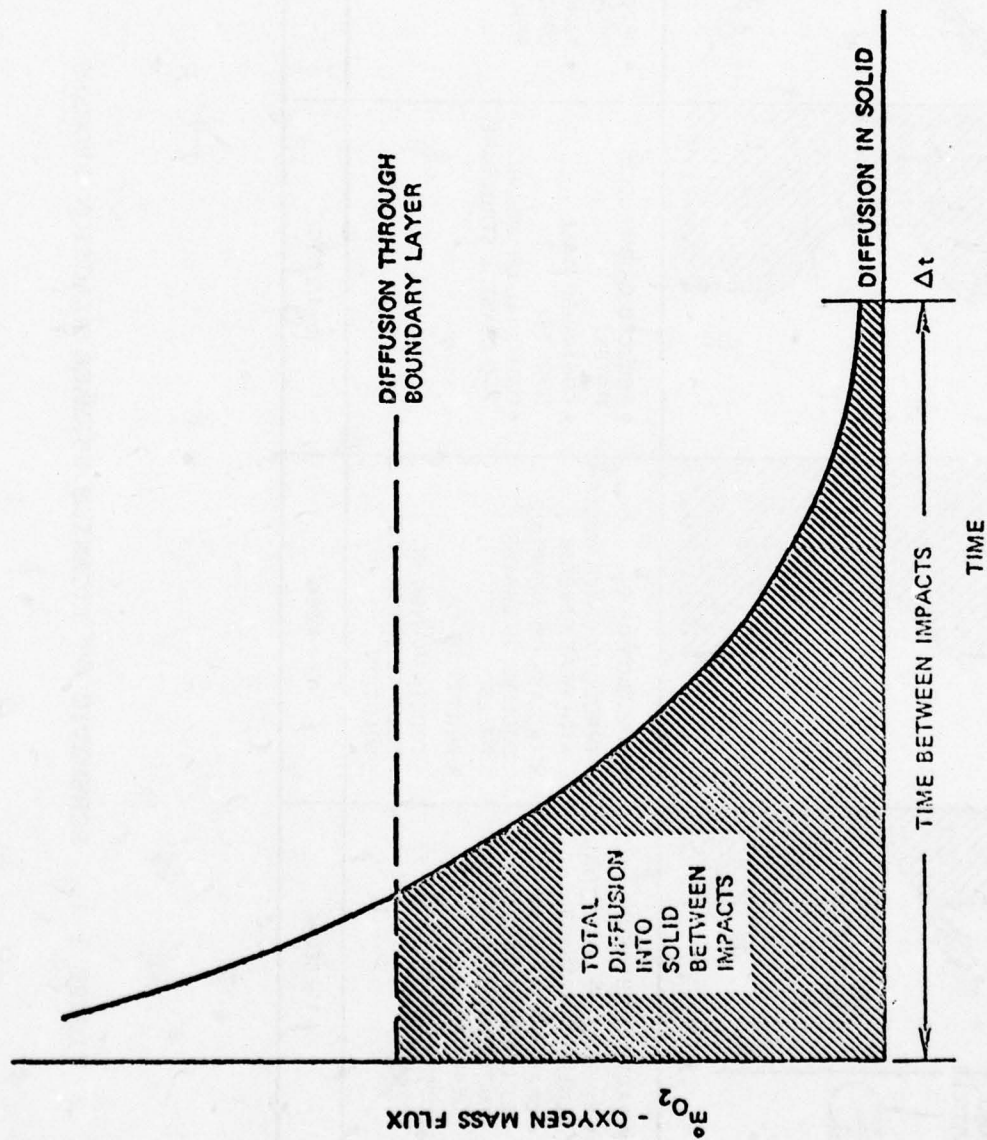


FIGURE 1-2. SCHEMATIC OF CONSTRAINTS ON OXYGEN MASS FLUX INTO SOLID TITANIUM

$$\dot{q}_{\text{react}} \sim C_s \Delta H_s \frac{1}{\sqrt{\tau}} \exp(-B/T)$$

where B is a constant and  $\tau = \frac{2 \rho_p d_p}{3 \rho_{CL} V \alpha}$  where  $\alpha$  is the ratio of projected crater surface area to particle cross-sectional area (order of 1),  $\rho_p$  is the particle density,  $d_p$  is the diameter, V is velocity and  $\rho_{CL}$  is the cloud concentration. This model is generally applicable for impacts of any particle type for oxygen diffusion into titanium from any oxygen source. The constants in the above relation must be determined for specific cases. For dust impacts on titanium in air environments, a suitable empirical relation was derived to be

$$\dot{q}_{\text{react}} = 47700 \frac{1}{\sqrt{\tau}} \exp(-23085/T(^{\circ}R)) \text{ Btu/ft}^2\text{-sec}$$

where T is assumed to be the local titanium surface temperature. A comparison of past AEDC DET data (4) with this model, shown in Figure 1-3, shows excellent agreement. The more generalized model for dust particle-titanium chemistry coupling provides a framework for considering the additional effects of ice impacts on titanium surface chemistry.

There are several unique differences between ice and dust impact conditions which could alter the titanium surface chemistry heating augmentation. Specific parameters affected include  $\tau$  (particle density, diameter and cloud density differences); T (different kinetic energy transfer and thus local crater temperature on impact);  $C_s$  (available concentration of oxygen in the boundary layer at the titanium surface); B (activation energy) and the rate constant for diffusion of water species into titanium.

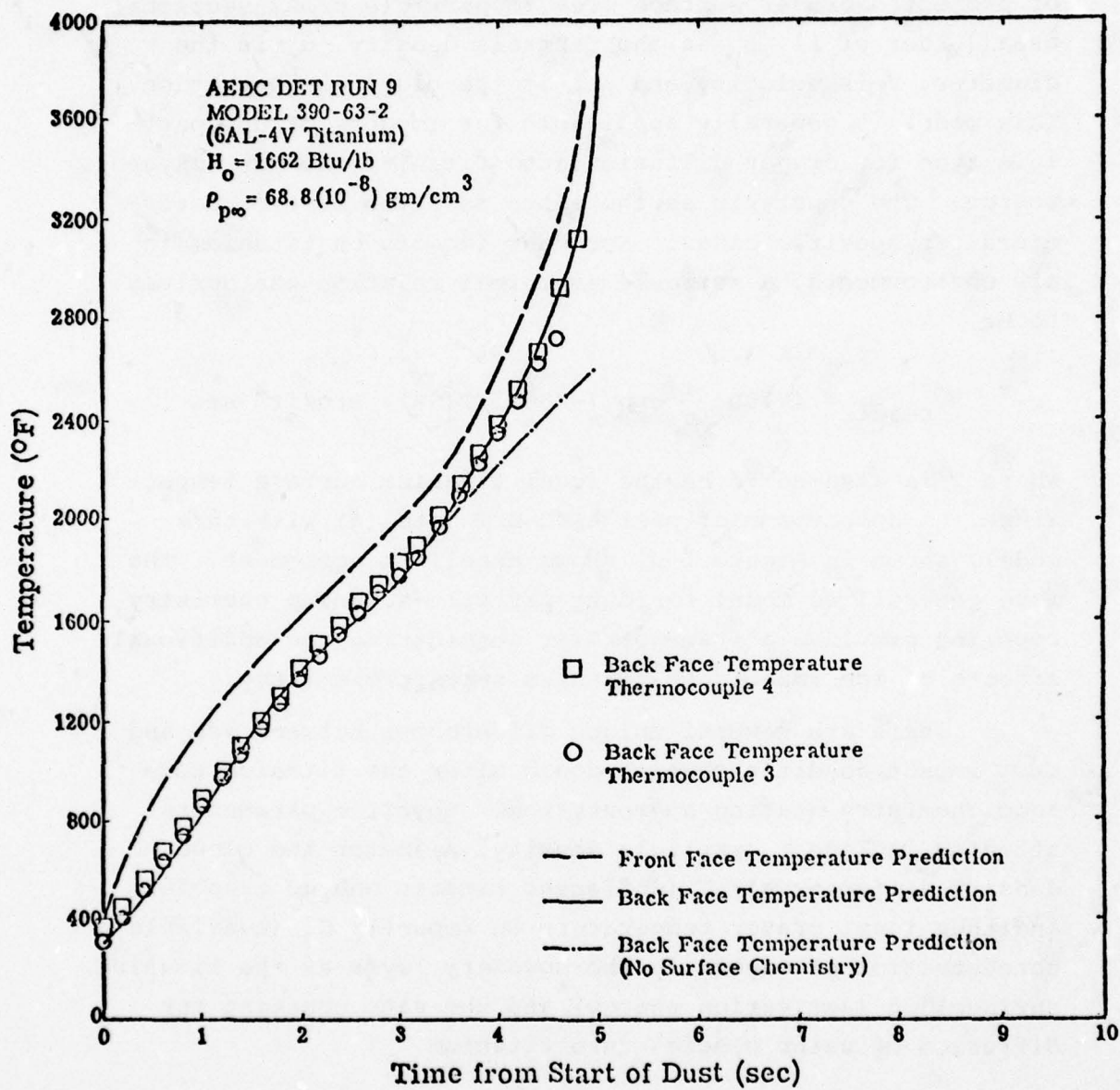


FIGURE 1-3. APPLICATION OF THE HEATING AUGMENTATION MODEL FOR AEDC DET RUN 9 (FROM REFERENCE 4)



The objective in this program was to obtain oxidation and impact test data for titanium at elevated temperatures in oxidizing environments to determine if the presence of ice or water significantly altered the response characteristics of titanium under dust impact conditions which were successfully modeled in previous studies. Test facilities selected were as follows:

1. SAI Oxidation Test Facility
2. SAI Ice Impact Test Facility
3. AEDC Dust Erosion Tunnel

No facility currently exists which can simulate multiple ice erosion on titanium in an oxidizing environment for time periods greater than a few milliseconds in order to evaluate chemistry effects. The above facilities simulate critical elements of the nuclear cloud ice/water and dust environment for evaluating a missile titanium component response. In addition to the test program, an improved analytical model was formulated for titanium oxidation based on data in the literature including limited data on the effect of steam oxidation of titanium. This model was used to analyze test data and evaluate the combined effects of ice/water and dust particle environments on titanium.

#### 1.2 Summary of Results

The results of this exploratory program show no significant overall degradation in titanium performance for combined ice/water and dust environments versus dust environments. Previous studies of titanium response to dust showed surface chemical reactions becoming important at temperatures in excess of 2000°F and eventually causing ignition at higher temperatures. This temperature of 2000°F remains a valid criteria for ice/water and dust below which

surface chemistry effects are unimportant. Ignition is not expected where the bulk temperature of the titanium is always below 2000°F.

Specific results from this program contributing to the above general conclusion include:

1. Titanium Oxidation Results

The SAI Phase I tests of titanium in non-erosive oxidizing environments ( $H_2O$  vapor and  $O_2$ ) showed an apparent increase in oxidation rate in  $H_2O$  vapor compared to  $O_2$  for temperatures of 1200-1500°K. At the 1700°K condition, this trend was not evident with  $O_2$  and  $H_2O$  vapor giving similar oxidation rates. Figure 1-4 shows a comparison of the Phase I experimental results with the oxidation model derived from the literature. The nominal model suggests a parabolic-type weight gain law ( $\Delta W/\sqrt{t}$ ) where  $\Delta W$  is the total weight gain and  $t$  is the total test time. The bulk of the test data (both  $H_2O$  vapor and  $O_2$ ) fall within the  $\pm$  factor of 2 uncertainty band for the  $O_2$  oxidation model based on data in the literature. The exception is the 1.0 atm data at 1400°K where a pressure effect is suggested. This was unexpected based on a solid-phase diffusion-controlled model and suggests the possibility that the SAI oxidation tests may have been gas-phase rate-limited although this was not confirmed during the testing. Although the  $H_2O$  vapor data from this program falls within the uncertainty band of the total experimental data base for  $O_2$  oxidation data from the literature, the current  $H_2O$  vapor data does indicate a general increase in oxidation compared to the current  $O_2$  data up to the 1700°K condition.

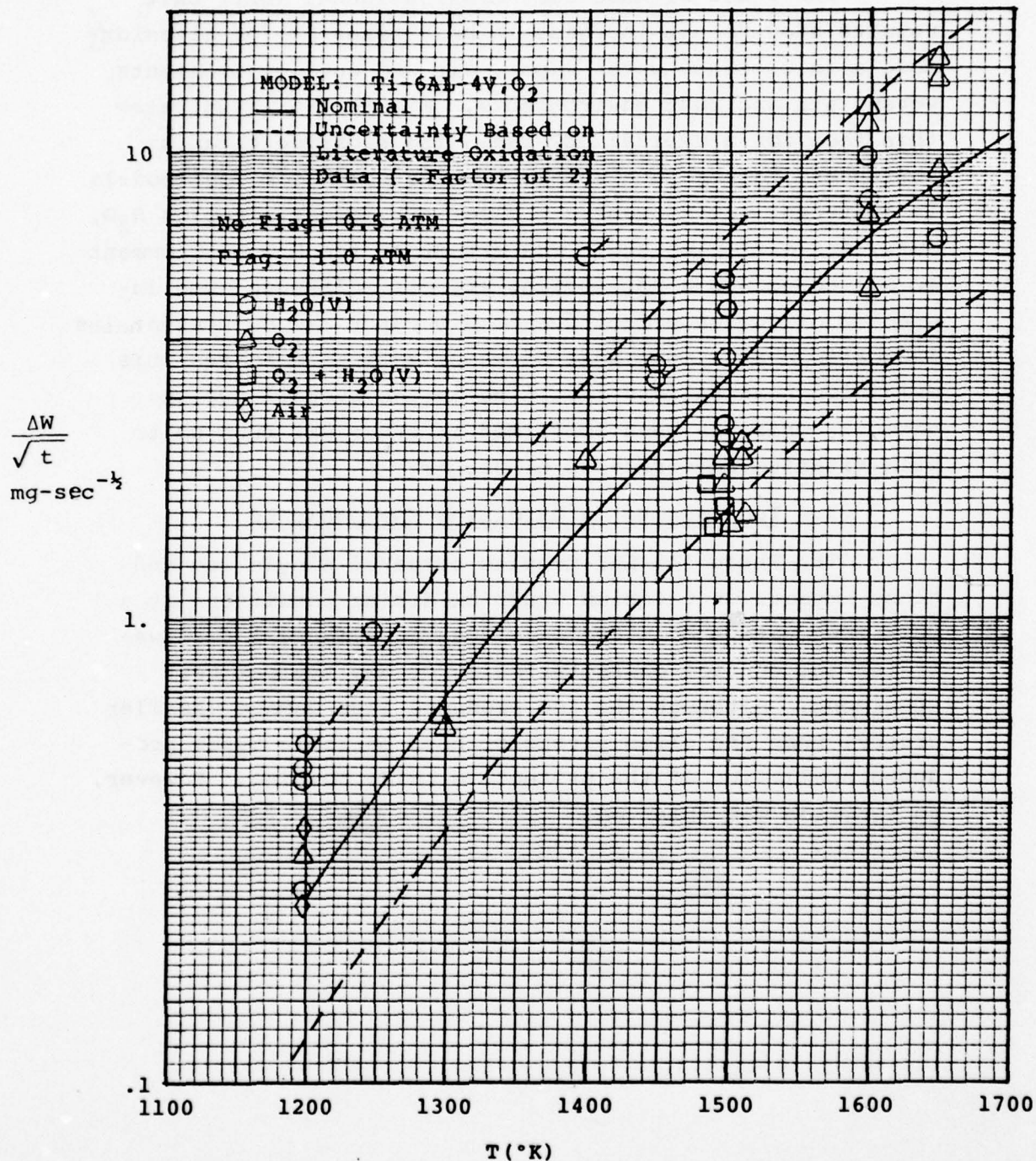


FIGURE 1-4. COMPARISON OF EXPERIMENTAL AND ANALYTICAL TITANIUM OXIDATION RESULTS



## 2. Combined Erosion and Oxidation

The Phase II AEDC Dust Erosion Tunnel (DET) test results show no net increase in heat transfer for titanium models in combined water vapor, air and dust environments versus air and dust environments. Figure 1-5 illustrates this fact for a typical DET run. The backface titanium hemisphere temperature versus time is shown for four models in different environments -- clear air, clear air plus  $H_2O$ , dust, and dust plus  $H_2O$ . The effect of the  $H_2O$  environment in all cases was a net cooling effect. Although some increased oxidation effect due to  $H_2O$  vapor may be present (as indicated above), the heat of vaporization dominates this oxidation heat release resulting in the overall cooling effect. This has been confirmed in other DET runs up to bulk titanium temperatures of 2500°F.

## 3. Ice Impacts in Oxidizing Environments

The Phase III SAI results compared single ice and glass impacts on titanium under oxidizing conditions at a bulk temperature of  $\sim 1700^\circ\text{F}$  ( $\sim 1200^\circ\text{F}$ ). Figure 1-6 illustrates the surface characteristics of two typical test specimens. Although the ice produced less damage (smaller crater) than the glass particle, both particle types produced spallation of the protective oxide coating. However, no ignition was observed.

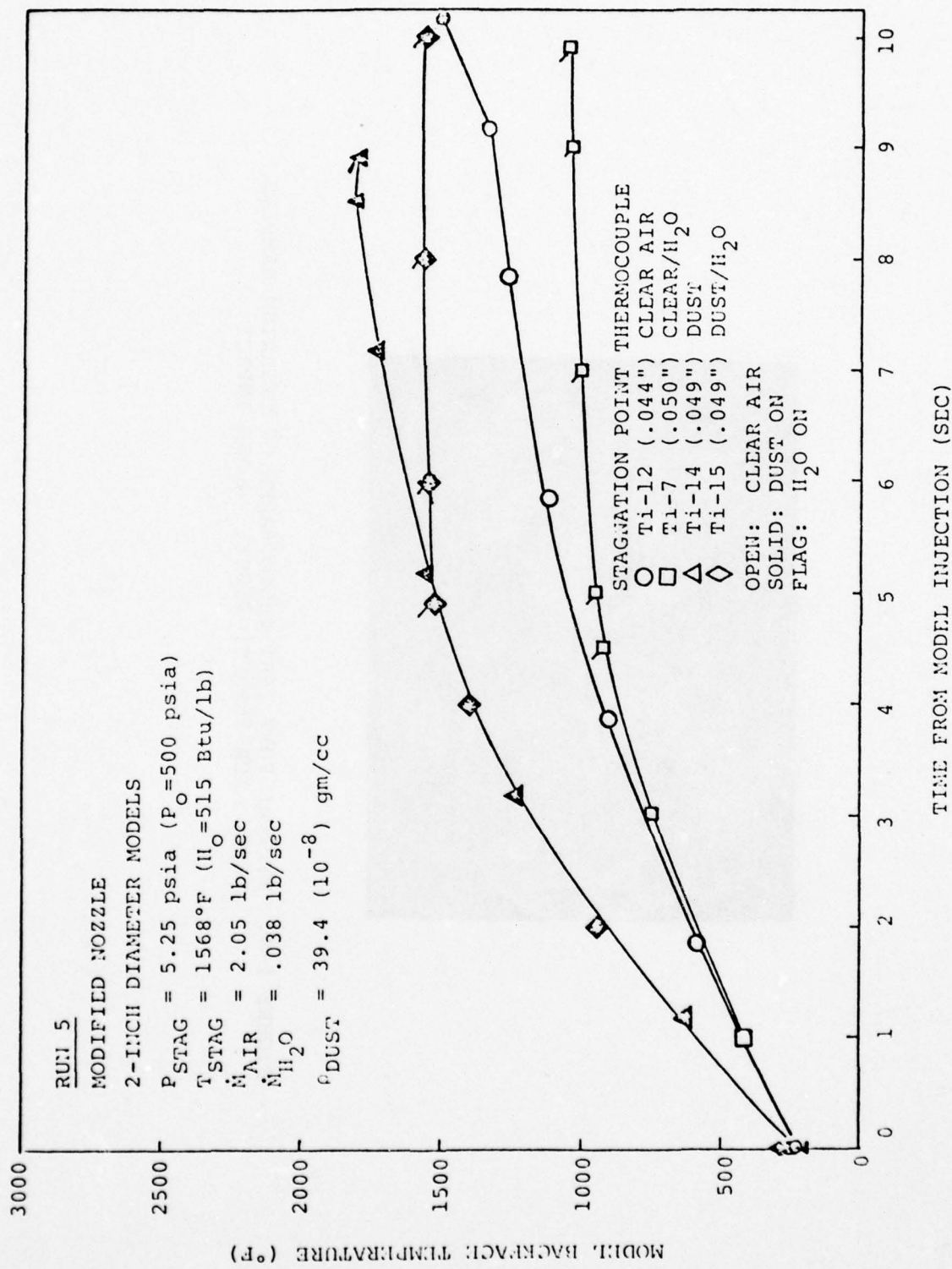


FIGURE 1-5. RESULTS FROM AEDC DET RUN 5

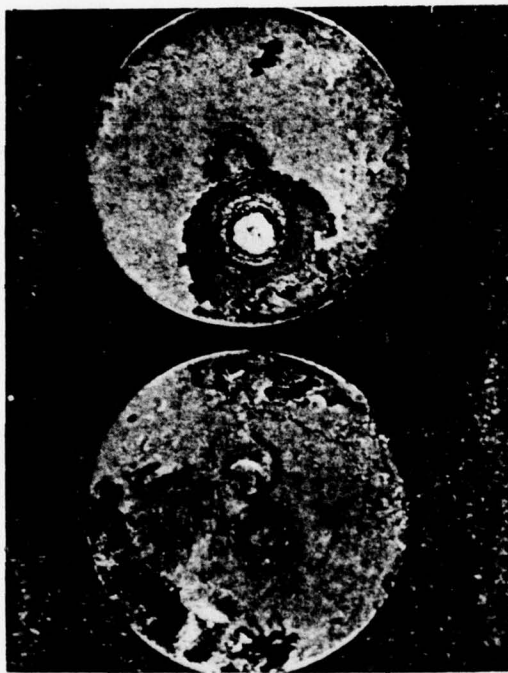


FIGURE 1-6. TYPICAL POST TEST PHOTOGRAPHS OF TITANIUM SAMPLES  
LEFT: ICE IMPACT, RIGHT: GLASS IMPACT



## 2.0 SAI OXIDATION AND IMPACT TEST SERIES

### 2.1 Test Objectives and Scope

The objectives of the Phase I oxidation tests were to evaluate the effect of water vapor and pressure on the oxidation characteristics of titanium (6AL-4V) at elevated temperatures. The scope of Phase I included three test series with a total of 36 tests using the oxidation test fixture at the SAI Santa Ana, California laboratory.

The objective of the Phase III impact tests was to evaluate titanium response to ice and glass impacts in oxidizing environments to determine if ignition occurs from single impacts. The scope of Phase III included six tests in the SAI impact facility at Santa Ana, California on 6AL-4V titanium at elevated temperature comparing glass and ice impact results.

### 2.2 Oxidation Test Program

The Phase I oxidation tests were conducted at the SAI Santa Ana, California laboratory in a test rig especially designed for this DNA program. The test rig is shown in Figure 2-1. The test specimen (see Figure 2-2) is suspended by thermocouple wires welded to the specimen in a vicor cylinder. An induction coil attached to the 25KW induction heater surrounds the vicor tube. The environment ( $O_2$ , air, argon,  $H_2O$  vapor, or mixtures) is controlled by admitting the respective gases to the test chamber via a control panel equipped with solenoid on-off valves and manually operated flow regulating valves.

The insitu instrumentation consisted of type E and type S thermocouples and an optical pyrometer to measure specimen temperature history. Pre-test and post-test weight measurements of the test sample and its thermocouple were performed to determine oxidation weight gain.

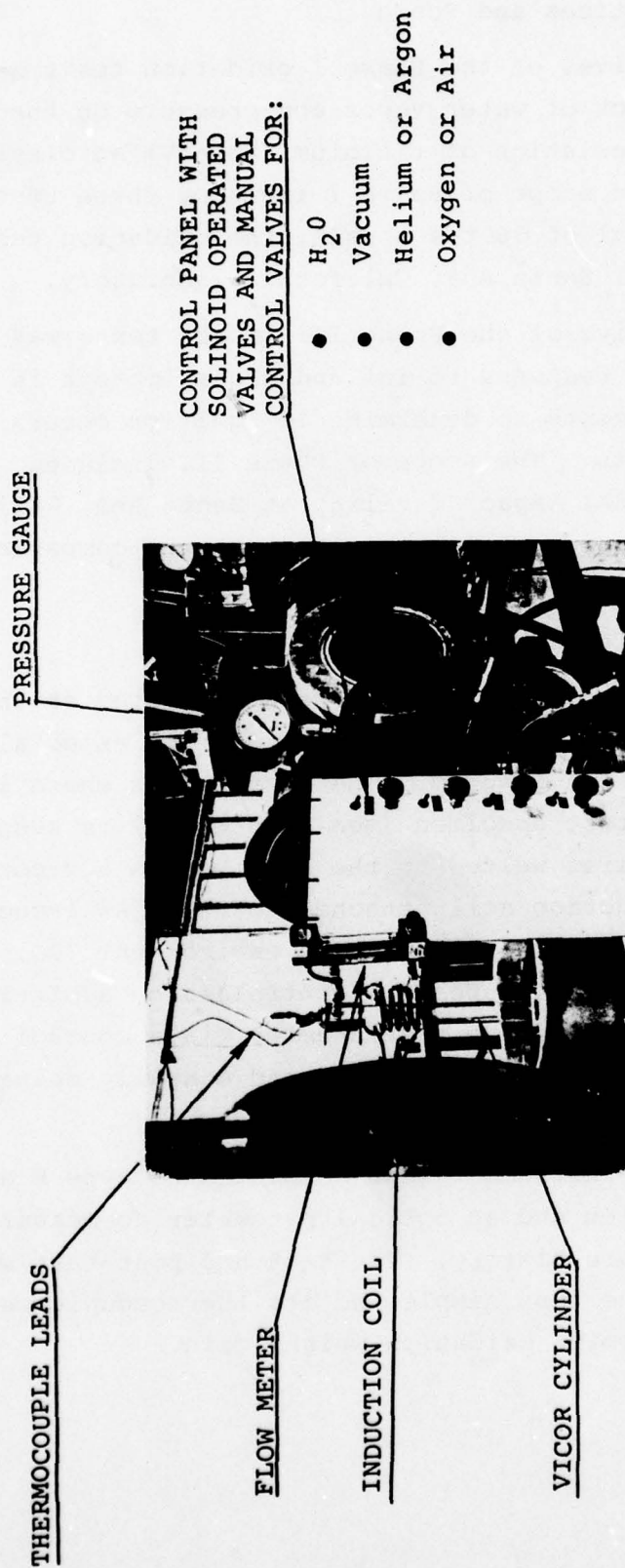


FIGURE 2-1a. OXIDATION TEST STAND - FRONT VIEW

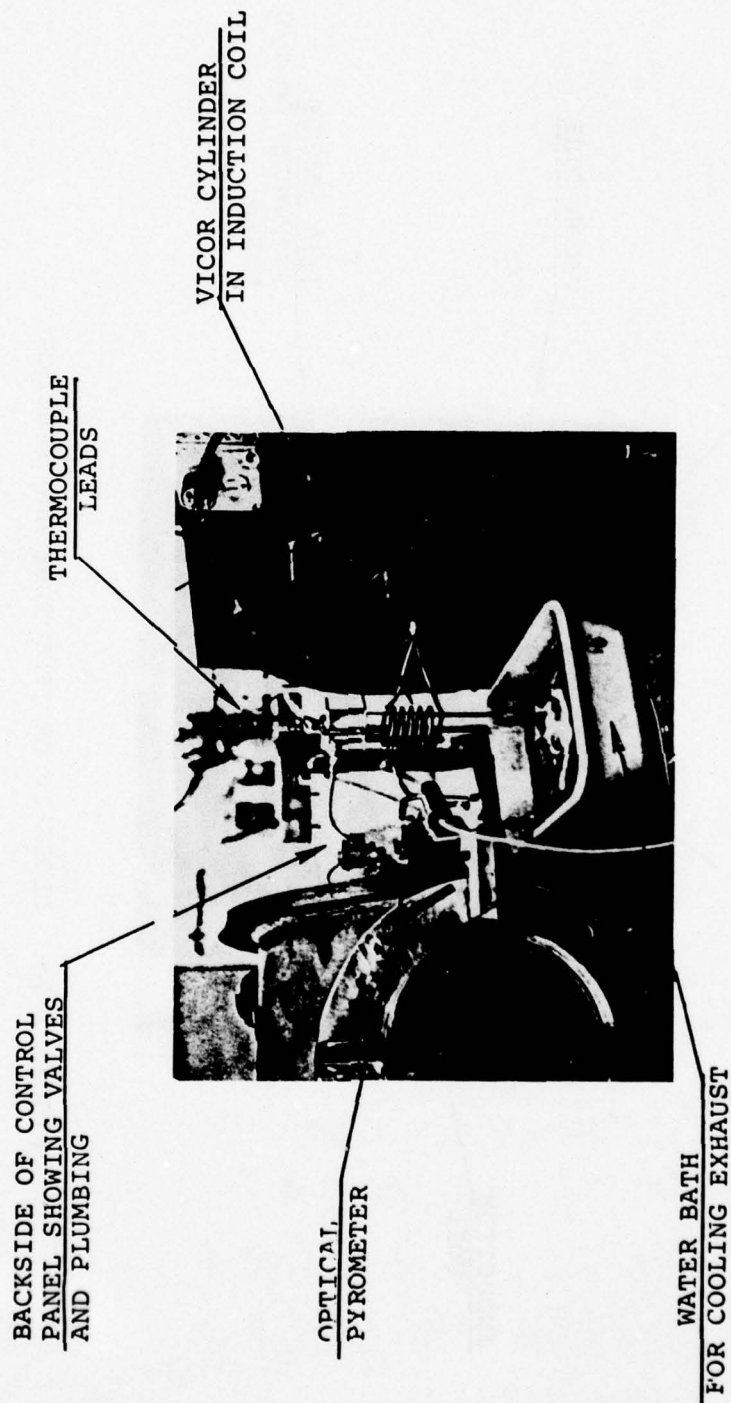


FIGURE 2-1b. OXIDATION TEST STAND - REAR VIEW



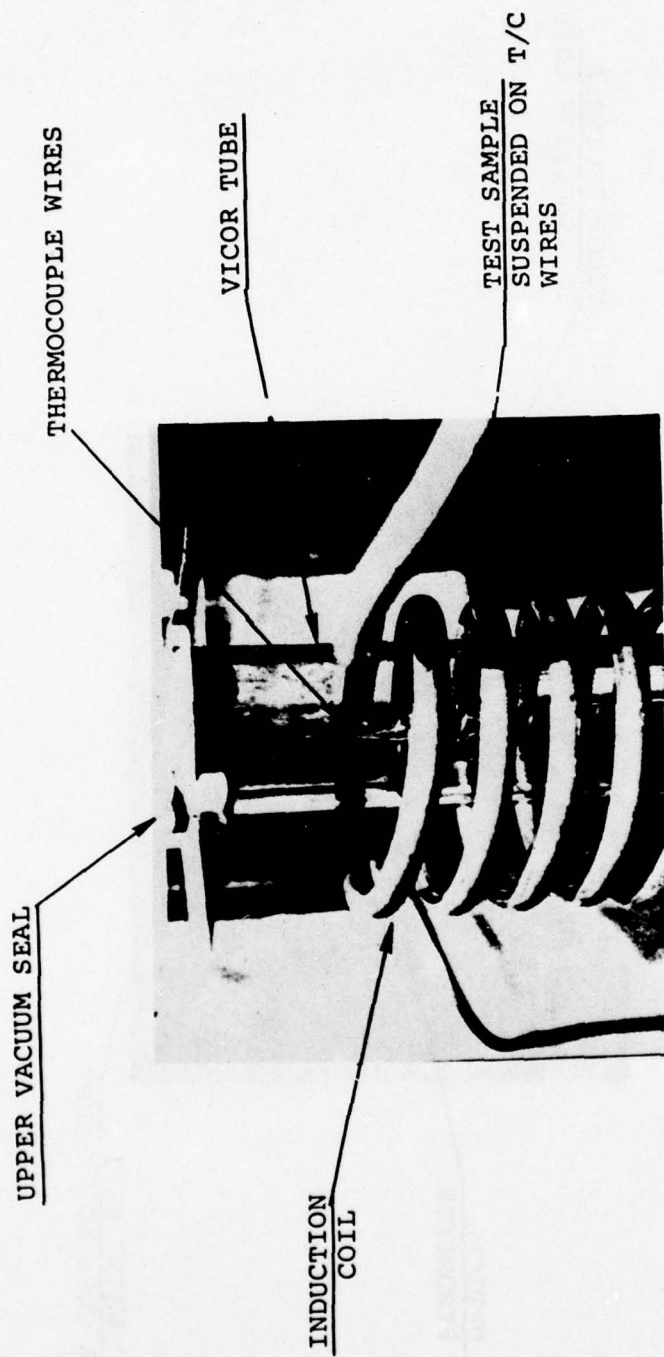


FIGURE 2-1c. CLOSE-UP OF TEST TUBE AND SPECIMEN

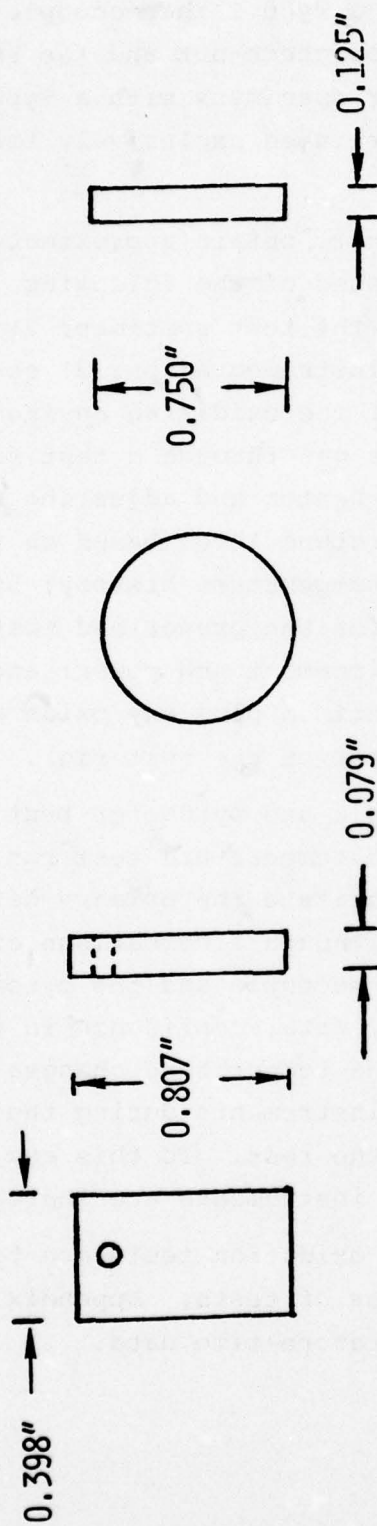
The test specimen configurations are shown in Figure 2-2. The disc configuration with a Type E thermocouple welded to the backface was used for check-out and the Phase III impact tests. The rectangular specimens with a Type S thermocouple welded to the end were used exclusively for the oxygen weight gain tests.

The test procedure followed to obtain approximately isothermal weight gain data consisted of the following steps: 1) a pre-test weighing of the test specimen; 2) installing the test specimen and instrumentation; 3) establishing the desired pressure of the oxidizing environment with a continuous flow of the same gas through a test fixture; 4) initiating the induction heater and adjusting the power to attain the desired temperature level based on real-time observation of the specimen temperature history; 5) maintaining constant temperature for the prescribed test time; 6) cut-off of oxidizing environment and power; and, 7) post-test weighing of the test specimen plus any oxide spall (captured in a catcher at the bottom of the test rig).

Figure 2-3 shows thermocouple and pyrometer test results for a typical low and high temperature test run. The thermocouple measurements constitute the primary data with the pyrometer as back-up. Although a comparison of the temperatures indicated by the thermocouple and the pyrometer is not possible without emissivity data, confidence in the data can be gained by comparing the temperature changes indicated by the two independent instruments during the "constant" temperature period of the test. To this end, the relative sensitivities of the two instruments are indicated.

The results of the Phase I oxidation tests are tabulated in Table 2-1 for three series of tests. Appendix B provides detailed tabulated temperature-time data.

(MTL, TI-6AL-4V)



RECTANGULAR CONF.

DISC CONF.

SPOT WELDS



THERMOCOUPLE  
WIRES

TYPICAL THERMOCOUPLE  
INSTALLATION

THERMOCOUPLE TYPES

Type S - Platinum vs Platinum-  
10% Rhodium

Type E - Nickel-Chromium vs  
Copper-Nickel

FIGURE 2-2. TYPICAL TEST MODEL CONFIGURATIONS



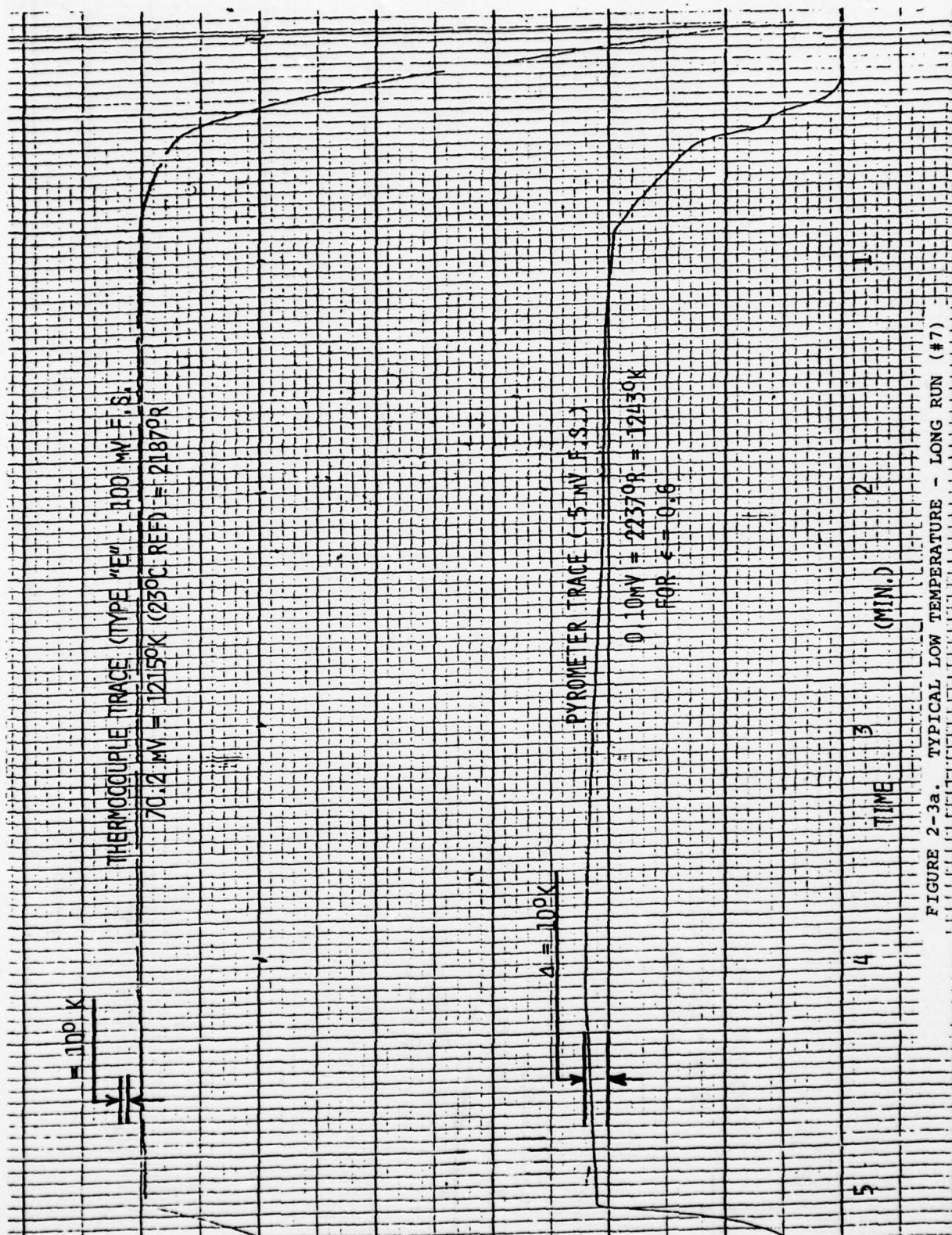


FIGURE 2-3a. TYPICAL LOW TEMPERATURE - LONG RUN (#7)

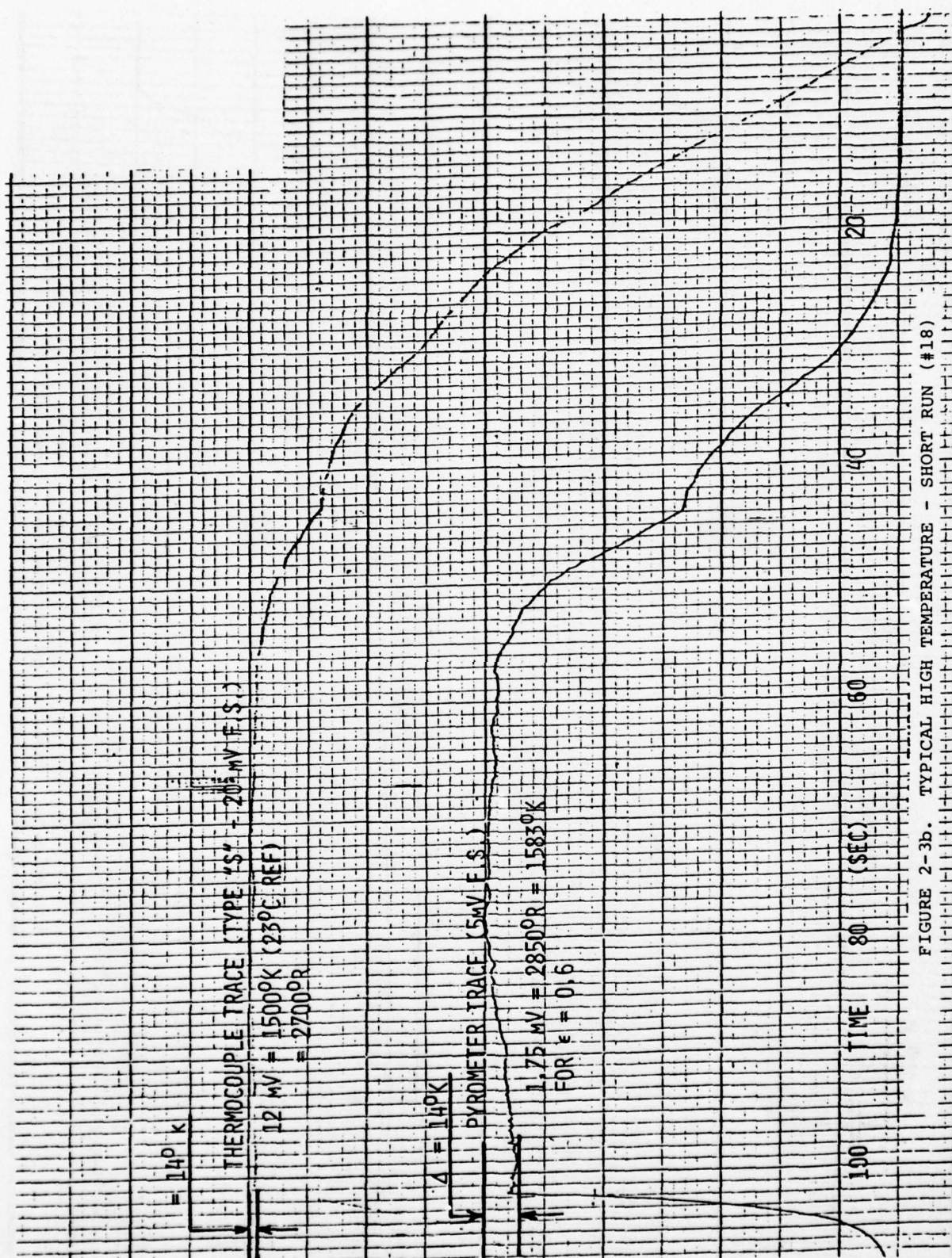


FIGURE 2-3b. TYPICAL HIGH TEMPERATURE - SHORT RUN (#18)



TABLE 2-1A

## TITANIUM OXIDATION RUN SUMMARY: SERIES 1, JANUARY 1977

RUN NO.	SAMPLE GEOMETRY	THERMOCOUPLE TYPE	NOMINAL TEMP (°K)	NOMINAL TIME (MIN)	PRESSURE (atm)	GAS COMPOSITION	WEIGHT GAIN (mg)	CHART SPEED	COMMENTS
4	Disc	E	1200	3	0.5	He	2.0	2"/m	
5	Disc	E	1200	3	0.5	He	1.4	2"/m	Good vacuum
6	Disc	E	1200	3	0.5	Arg.	2.0	2"/m	
7	Disc	E	1200	5	0.5	O <sub>2</sub>	7.2	2"/m	Start heat in O <sub>2</sub>
8	Disc	E	1200	1.5	0.5	O <sub>2</sub>	1.6	2"/m	Noisy trace
9	Rect	S	1000	10	0.5	O <sub>2</sub>	1.1	2"/m	Did not reach 1200 only 1000. Must re-set machine for high.
10	Rect	S	1200	5	0.5	O <sub>2</sub>	5.4	2"/m	Had arc-over
11	Rect	S	1500	1.5	0.5	O <sub>2</sub>	22.7	6"/m	Temp overshoot to ~1600
12	Rect	S	1500	1.5	0.5	H <sub>2</sub> O	35 +	6"/m	Lost some flakes
15	Rect	S	1200	~7	0.5	H <sub>2</sub> O	5.4	6"/m	
16	Rect	S	1200	5	0.5	Air	4.2	6"/m	Strip chart not available
17	Rect	S	1200	5	0.1	Air	6.2	6"/m	Strip chart not available
18	Rect	S	1500	1.5	0.5	50/50H <sub>2</sub> O-Air	15	6"/m	Some flakes lost



TABLE 2-1B

TITANIUM OXIDATION RUN SUMMARY: SERIES 2, MAY 1977						
RUN NO.	NOMINAL TEMP (° K)	NOMINAL TIME (SEC)	PRESSURE (atm)	GAS COMPOSITION	WEIGHT GAIN (mg)	COMMENTS
2	1500	100	0.5	O <sub>2</sub>	16.15	No scale catcher in setup
3	1500	100	0.5	O <sub>2</sub>	19.74	No scale catcher in setup
4	1600	100	0.5	O <sub>2</sub>	73.75	
7	1650	50	0.5	O <sub>2</sub>	101.76	
8	1500	100	0.5	H <sub>2</sub> O(v)	46.57	Baked out weight less 1.7 mg
9	1500	100	0.5	O <sub>2</sub>	22.34	
10	1450	100	0.5	H <sub>2</sub> O(v)	35.22	Temp lower than 1500° K
11	1500	120	0.5	O <sub>2</sub> H <sub>2</sub> O(v)	18.82	Mix of gases uncertain, significant pressure change
12	1500	100	0.5	O <sub>2</sub> H <sub>2</sub> O(v)	19.66	Mix of gases uncertain, significant pressure change
15	1500	50	0.5	O <sub>2</sub>	11.97	
17	1650	60	0.5	O <sub>2</sub>	70.39	Temperature slightly low
18	1650	60	0.5	H <sub>2</sub> O(v)	50.90	Temperature too low
19	1650	60	0.5	H <sub>2</sub> O	63.20	Temperature too low
20	1200	300	0.5	H <sub>2</sub> O(v)	8.56	
21	1200	300	0.5	H <sub>2</sub> O(v)	8.10	
22	1500	35	1.0	O <sub>2</sub>	-	Specimen ignited
24	1400	50	1.0	O <sub>2</sub>	15.80	
25	1400	65	1.0	H <sub>2</sub> O(v)	50.63	

NOTE: All specimens 1 cm x 2 cm x 0.2 cm, Mass = 1.8 gms. Thermocouples Type S.  
Reference Temperature, 18°C. Chart speed 0.1 in/sec.

TABLE 2-1c  
TITANIUM OXIDATION RUN SUMMARY: SERIES 3 JULY 1977

RUN NO.	NOMINAL TEMP (°K)	NOMINAL TIME (SEC)	PRESSURE (ATMOSPHERE)	GAS COMP.	WT. GAIN (mg)	COMMENTS
26	1500	60	0.5	H <sub>2</sub> O	20.4	• time more like 58-63 sec but steady temp. - good run
27	1450	95	1.0	H <sub>2</sub> O	31.2	• ~ 53 sec at 1500°K but additional 35 sec init at ~ 1400°K! No good
28	1500	55	1.0	H <sub>2</sub> O	40.0	• ~ 53-60 sec and steady good run.
29	1200	150	0.5	H <sub>2</sub> O	6.8	• Temp overshoot init ~ 40 sec
31	1600	70	0.5	H <sub>2</sub> O	65.8	• Temp low most of run, more like ~ 70 sec @ 1600°K
32	1600	80	0.5	H <sub>2</sub> O	89.1	• Temp low-more like 80 sec @ 1600°K slightly higher levels to run 31 however higher pressure may cause high AW
33	1600	60	0.5	O <sub>2</sub>	90.8	• Temp erratic (low) time about 60 sec @ ~ 1600°K
34	1600	70	0.5	O <sub>2</sub>	102.4	• Stable Temp not achieved, low temp ~ 70 sec @ 1600°K
35	1650	60	0.5	O <sub>2</sub>	120.7	• 1700°K maintained for only 10 sec -- ~ 60 sec total, most @ 1500°K+, no good
36	1600	50	0.5	O <sub>2</sub>	35.6	• Overshoot to nearly 1700° ~ 30 sec @ ~ 1400°K, ~ 22 sec above 1500°K No good
37	1500	50	1.0	O <sub>2</sub>	15.9	• Good run 50 sec @ ~1500°K
38	1500	50	1.0	O <sub>2</sub>	16.7	• Slight overshoot for 1st 10 sec to ~1550°K and undershoot for last 40 sec to ~1450°K, good
39	1370	300	0.5	O <sub>2</sub>	10.8	• Temp overshoot ah ave. of ~1300°K for entire 300 sec
40	1300	300	0.5	O <sub>2</sub>	10.1	• Temp overshoot an ave. of ~1300°K for entire 300 sec
41	1700	-	0.5	O <sub>2</sub>	-	• Ignited at 5 sec, straggle to response above 1500°K
42	1250	300	0.5	H <sub>2</sub> O	17.0	• Temp 1200-1300°K, good

The interpretation of the data and the identification of specific trends is deferred to Section 4 where the data is presented in light of predictive oxidation models. Two general observations which can be made from the raw data are depicted in Figure 2-4 where results obtained at 1500°K are presented. A significant increase in oxygen uptake is seen for tests in water over tests in pure oxygen at 1500°Kelvin. A similar trend was observed at 1200°K, however, no difference was measured at 1700°K. It is also surprising to note that data obtained with a 50 percent mixture of oxygen and water vapor agreed with data obtained in pure oxygen at all temperatures tested. Unfortunately, the limited data generated does not permit any conclusions to be drawn from these observations.

For the two pressure levels tested, namely 1/2 and 1 atmosphere, both water and oxygen data suggest an increase in oxygen uptake with increasing pressure. This trend was unexpected although reported once in Ref. 10 since gas phase diffusion cannot be important in a single component atmosphere. As will be discussed in Section 4.0, this pressure effect may result from gas phase rate-limiting processes as opposed to any basic change in the solid phase oxidation or dissolution processes.

During the Series 2 and 3 tests conducted under this program, two titanium samples ignited and were consumed. The conditions for these tests were 1500°K, 1 atm O<sub>2</sub> and 1700°K, .5 atm O<sub>2</sub>. Examination of all available data on sample response and facility performance parameters revealed that in each case, the induction heater plate current, a measure of power delivered, increased spontaneously at the time the sample ignited. It cannot be stated with certainty if the ignition process proceeded and caused the abnormal induction heater response or if the induction heater



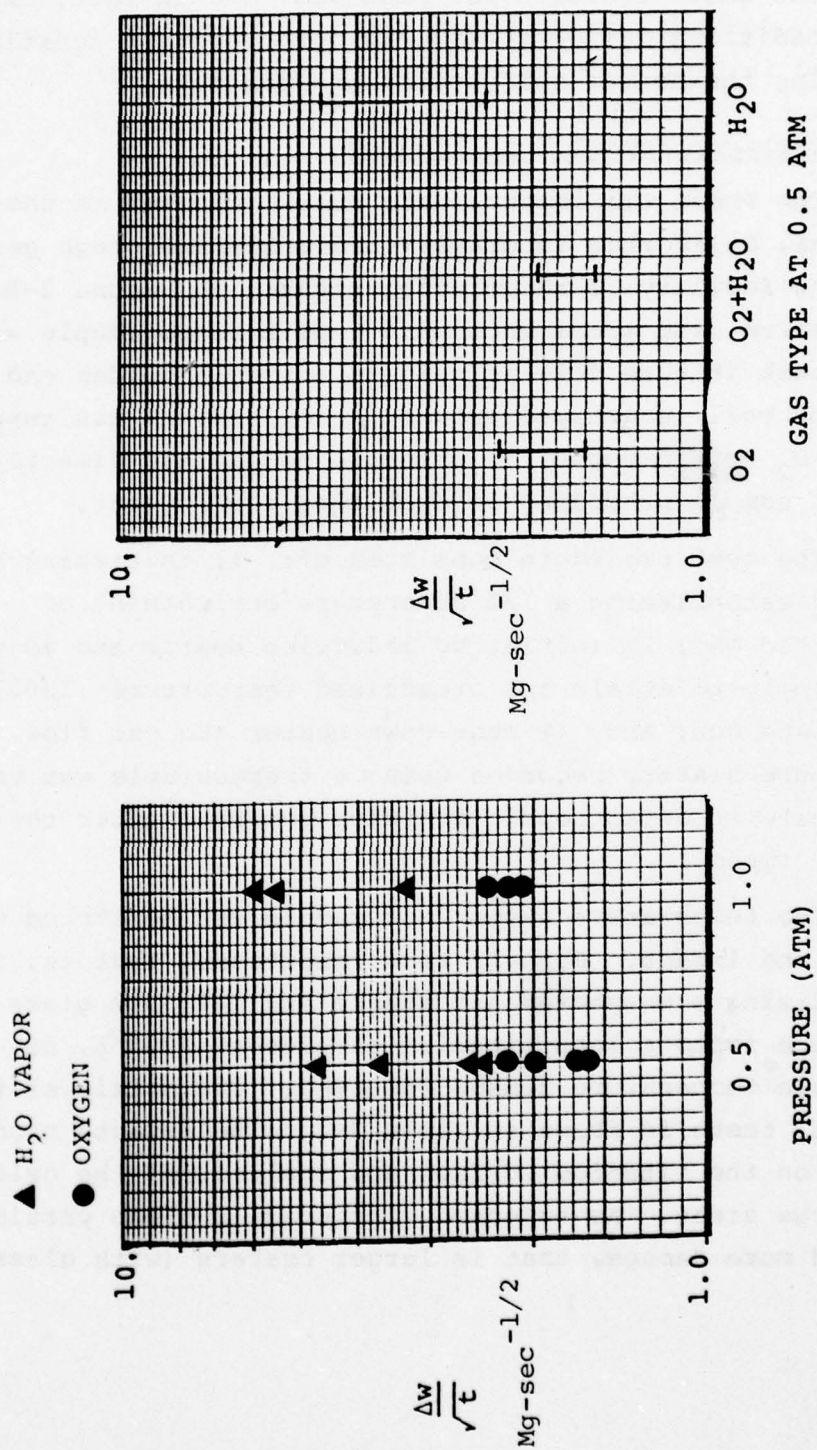


FIGURE 2-4. OXIDATION DATA TRENDS AT 1500°K

malfunctioned and caused the sample to ignite. Such heater malfunction is not likely but possible. Repeats of the test conditions where ignition was observed, and in fact, exceeding these conditions deliberately, did not result in ignition supporting the heater malfunction explanation.

### 2.3 Particle Impact Test Program

The Phase III impact tests were conducted at the SAI Santa Ana, California laboratory using the two-stage gas gun. The facility is shown schematically in Figure 2-5. The titanium disc specimen with a Type E thermocouple welded to the back (Figure 2-2) is held in a sample holder and the induction coil is wrapped around the holder. A gas supply line (either O<sub>2</sub> or H<sub>2</sub>O vapor) is oriented to impinge directly on the test sample providing an oxidizing environment.

The test procedure consisted of: 1) initiating gas flow and establishing a 1/2 atmosphere environment of the desired gas; 2) initiating induction heater and adjusting power supply to attain the prescribed temperature (1200°K); 3) initiate gun; and, 4) shut-down heater and gas flow. The temperature history recorded using a thermocouple was used to evaluate if catastrophic ignition occurred after the particle impact.

The temperature history of sample was monitored during heat-up and impact. For all test conditions, that is, inert and oxidizing atmospheres and single and multiple glass and single ice impacts into titanium samples at 1200°K, no measurable temperature damage resulted. The matrix of the Phase III tests is shown in Table 2-2. The impacts produced craters on the titanium surface and spalled off the oxide layers over large areas. As expected, the heavier glass particles produced more damage, that is larger craters (with glass residue

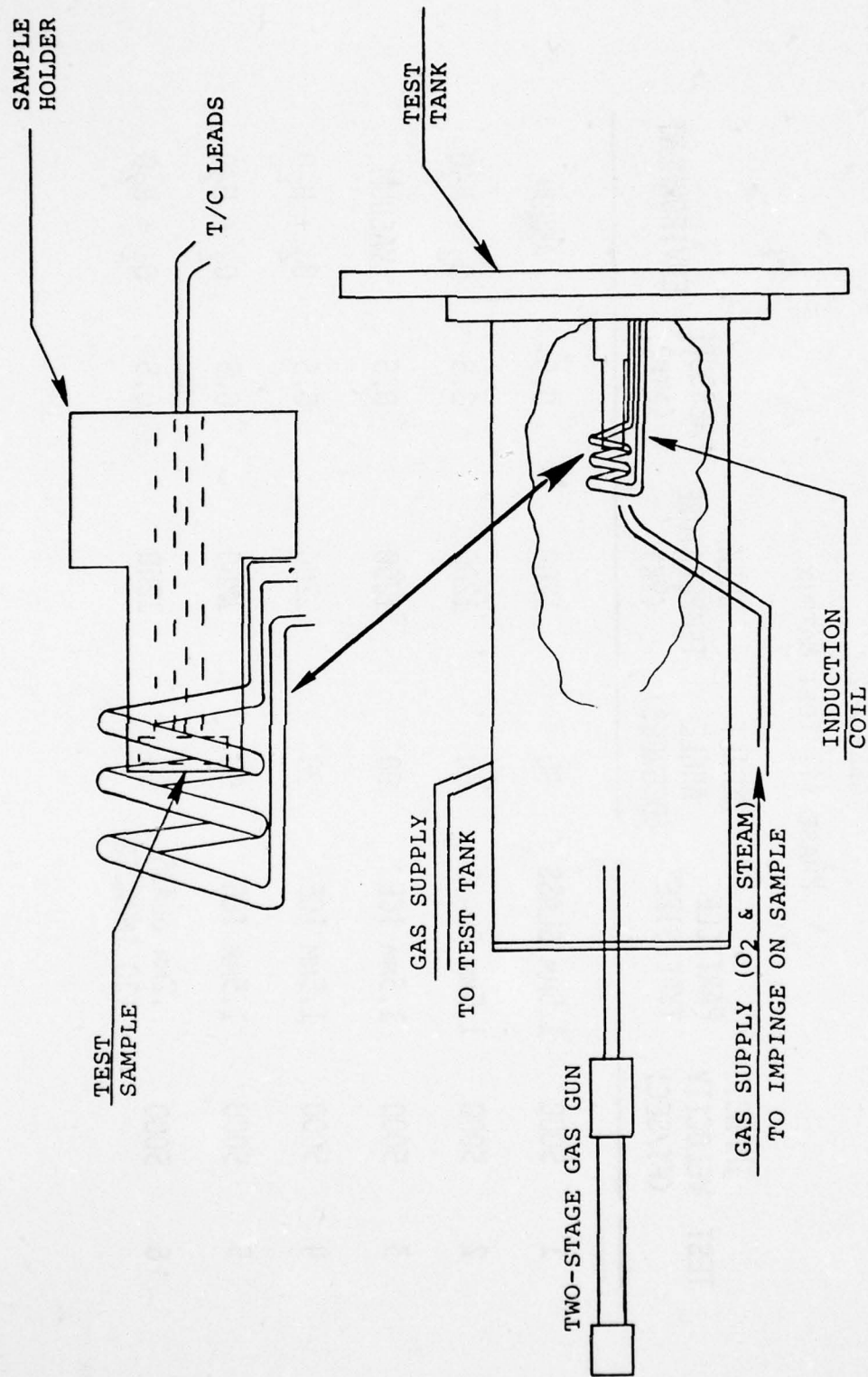


FIGURE 2-5. FACILITY SCHEMATIC FOR IMPACT/OXIDATION EXPERIMENTS



TABLE 2-2

## PHASE III TEST MATRIX

TEST	IMPACT VELOCITY (FT/SEC)	PARTICLE TYPE/SIZE	IMPACT ANGLE (DEGREES)	BULK TEMPERATURE (°K)	PRESSURE (ATM)	ENVIRONMENT
1	5000	1.5MM GLASS	90	1200	0.5	ARGON
2	5000	1.5MM GLASS	90	1200	0.5	O <sub>2</sub> + H <sub>2</sub> O
3	5000	1.5MM ICE	90	1200	0.5	VACUUM
4	5000	1.5MM ICE	90	1200	0.5	O <sub>2</sub> + H <sub>2</sub> O
5	5000	1.5MM ICE	90	1200	0.5	O <sub>2</sub> + H <sub>2</sub> O
6	5000	.2MM GLASS (20 IMPACTS)	90	1200	0.5	O <sub>2</sub> + H <sub>2</sub> O

in the crater bottom) and larger spall regions than the ice particle. A comparison of two typical craters resulting from ice and glass impact is shown in the post test photograph of Figure 2.6.

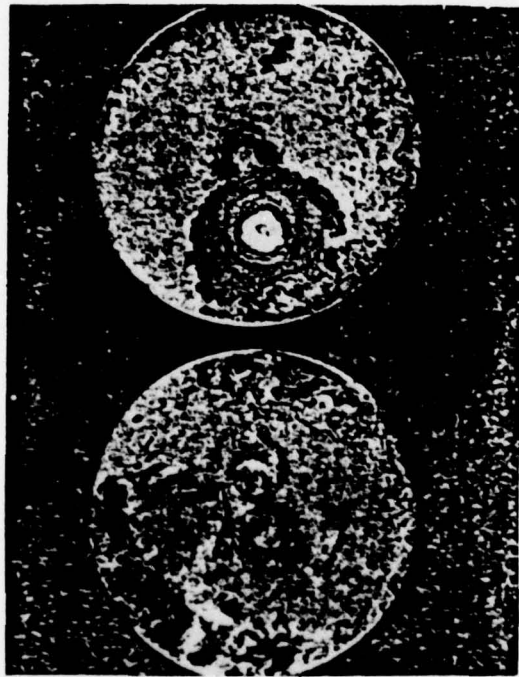


FIGURE 2-6. TYPICAL POST TEST PHOTOGRAPHS  
OF TITANIUM SAMPLES  
LEFT: ICE IMPACT, RIGHT: GLASS IMPACT



### 3.0 AEDC DET EROSION AND OXIDATION TEST SERIES

#### 3.1 Background

The test results described in the preceding section show the effect of oxidizing environments ( $H_2O$  vapor and  $O_2$ ) on titanium under both non-erosive and single impact test conditions using both non-reactive (glass) and reactive (ice) particles. This data is fundamental to the development of a predictive model for titanium response as will be discussed in Section 4.0. However, the test conditions are not representative of the multiple impact, hypersonic flow environment expected for a missile structure in-flight. Consequently, a test series was planned which would use the AEDC Dust Erosion Tunnel (DET) to evaluate titanium response to multiple particle impacts in a hypersonic flow environment. A facility modification was implemented to introduce liquid water simultaneously with dust (magnesium oxide) particles in an attempt to simulate the nuclear cloud water and dust environment.

Extensive tests of titanium nosetip models have been conducted in the DET in previous programs (References 1-5). These tests have been conducted to evaluate increased heat transfer in particle environments. Important mechanisms include particle kinetic energy transfer, particle-flowfield interaction convective heat transfer, and high temperature chemistry heating augmentation due to surface oxidation. These effects have been adequately modeled for dust particle/air environments. However, the effect of water, in the form of ice, liquid, or vapor in conjunction with a dust/air environment, on titanium has not been addressed. The concern was that water could increase the surface chemistry effect on titanium under erosive conditions and should be considered in the design of titanium missile structures. This AEDC DET test program was structured to evaluate this concern.

### 3.2 Test Objectives

A test program was planned for the AEDC DET to investigate the effects of water/air mixtures on the oxidation response of titanium under multiple dust particle conditions. Although the DET is used routinely for dust erosion testing, water had not been injected prior to this program. A facility modification was implemented to inject liquid water either separately or in combination with dust (MgO) particles. The goal was to achieve liquid water droplet impacts on the hemispherical titanium models which had been heated to high temperature by the hypersonic air and dust flow. This test program was the first such utilization of the AEDC DET and was necessarily exploratory in nature.

### 3.3 Test Program Description

#### 3.3.1 Facility Description

The tests were conducted in the Arnold Engineering Development Center, Propulsion Wind Tunnel Facility, Dust Erosion Tunnel (DET). A description of the DET is given in Reference 6. All test runs were made at the 127.5-in. nozzle station, where the exit diameter is 8.3 in. and the nominal Mach number is  $M = 6.6$  to 7.5, depending on operating conditions. A facility modification was designed and implemented to inject liquid water simultaneously with the dust particles. A schematic of the water/dust injection strut is shown in Figure 3-1. A separate water injection system was designed. The water injection line is shown in Figure 3-1 next to the dust injection line. Various orifices on the water injection line were evaluated to obtain the desired flow conditions.

#### 3.3.2 Water Orifice Calibration

A series of bench tests were performed to calibrate the water orifice. Four designs for the orifice were evaluated. The objective of the calibration tests was to obtain

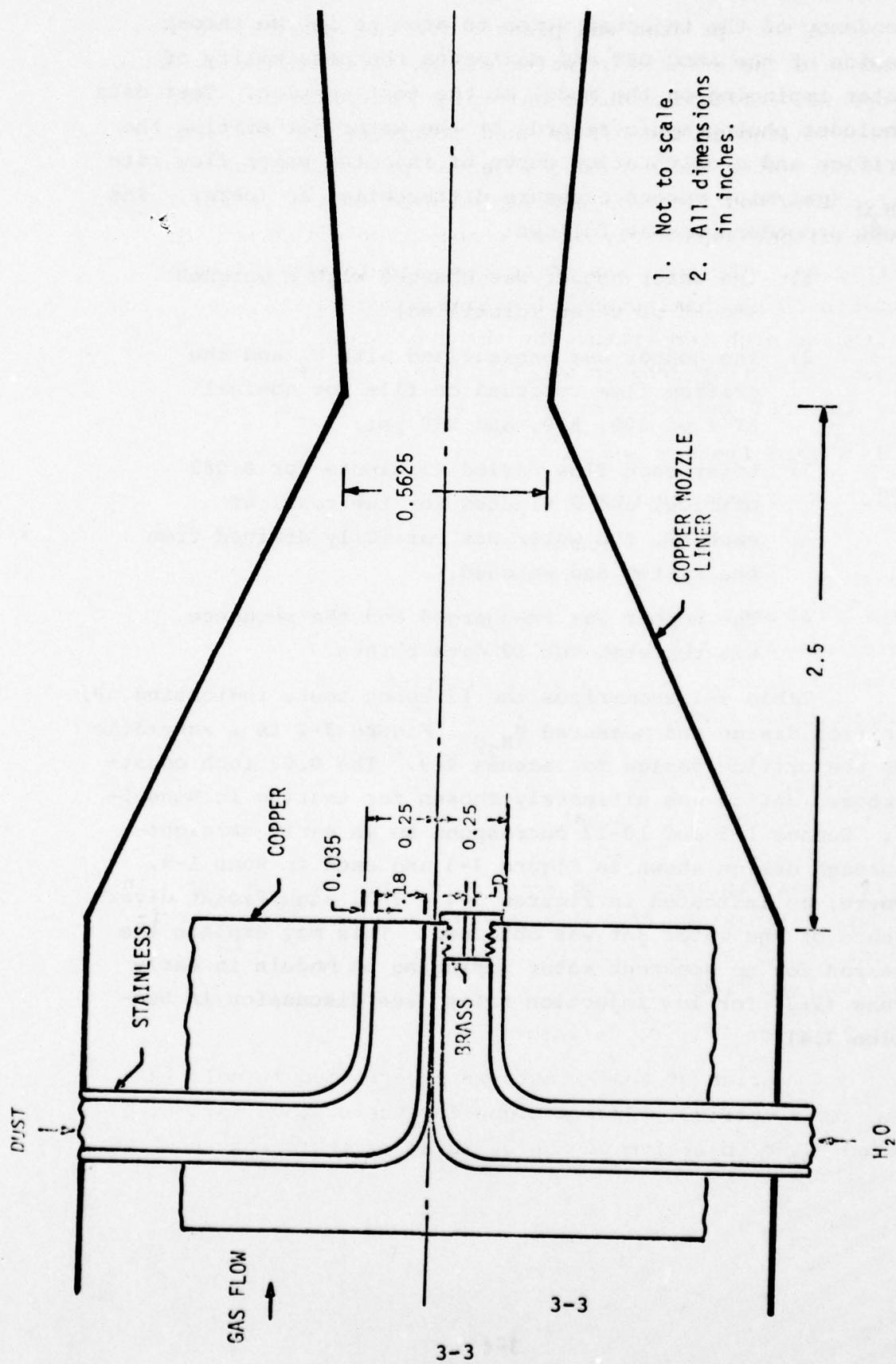


FIGURE 3-1. WATER/DUST INJECTION STRUT SCHEMATIC



a water jet with minimum divergence. This minimizes the tendency of the injected water to atomize in the throat region of the AEDC DET and maximizes the possibility of water impinging on the model at the test section. Test data includes photographic records of the water jet exiting the orifice and a calibration curve of injected water flow rate  $\dot{M}_{H_2O}$  (gal/min) versus pressure differential  $\Delta P$  (psia). The test procedure was as follows:

- 1) The water hopper was charged with a weighed amount of water (distilled).
- 2) The hopper was pressurized with  $N_2$  and the orifice flow recorded on film for nominal  $\Delta P$ 's of 200, 500, and 800 psi.
- 3) After each flow period (1 minute for 0.062 orifice, and 2 minutes for the rest) at each  $\Delta P$ , the water was carefully drained from the system and weighed.
- 4) The hopper was re-charged and the sequence was repeated for 12 data points.

Table 3-1 summarizes the 12 bench tests indicating  $\Delta P$ , orifice design and measured  $\dot{M}_{H_2O}$ . Figure 3-2 is a schematic of the orifice design for scenes 4-9. The 0.02 inch counter-bored design was ultimately chosen for testing in Runs 5-8. Scenes 1-3 and 10-12 correspond to an early straight-through design shown in Figure 3-3 and used in Runs 1-4, where, as indicated in Figures 3-4 - 3-7, significant divergence of the water jet was obtained. This may explain the reason for no apparent water impinging on models in early runs (1-3) for low injection rates (see discussion in Section 3.4).

TABLE 3-1

## WATER ORIFICE CALIBRATION

SCENE	NOM. $\Delta P$ , PSI	ORIFICE DIA, in	COUNTER BORED EXIT	CONICAL INLET	FLOW RATE, GPM
1	200	.0625	NO	YES	1.34
2	500	↓	↓	↓	2.07
3	800	↓	↓	↓	2.68
4	200	.040	YES	YES	0.56
5	500	↓	↓	↓	0.88
6	800	↓	↓	↓	1.18
7	200	.020	YES	YES	0.16
8	500	↓	↓	↓	0.25
9	800	↓	↓	↓	0.33
10	200	.020	NO	NO	0.15
11	500	↓	↓	↓	0.22
12	800	↓	↓	↓	0.28

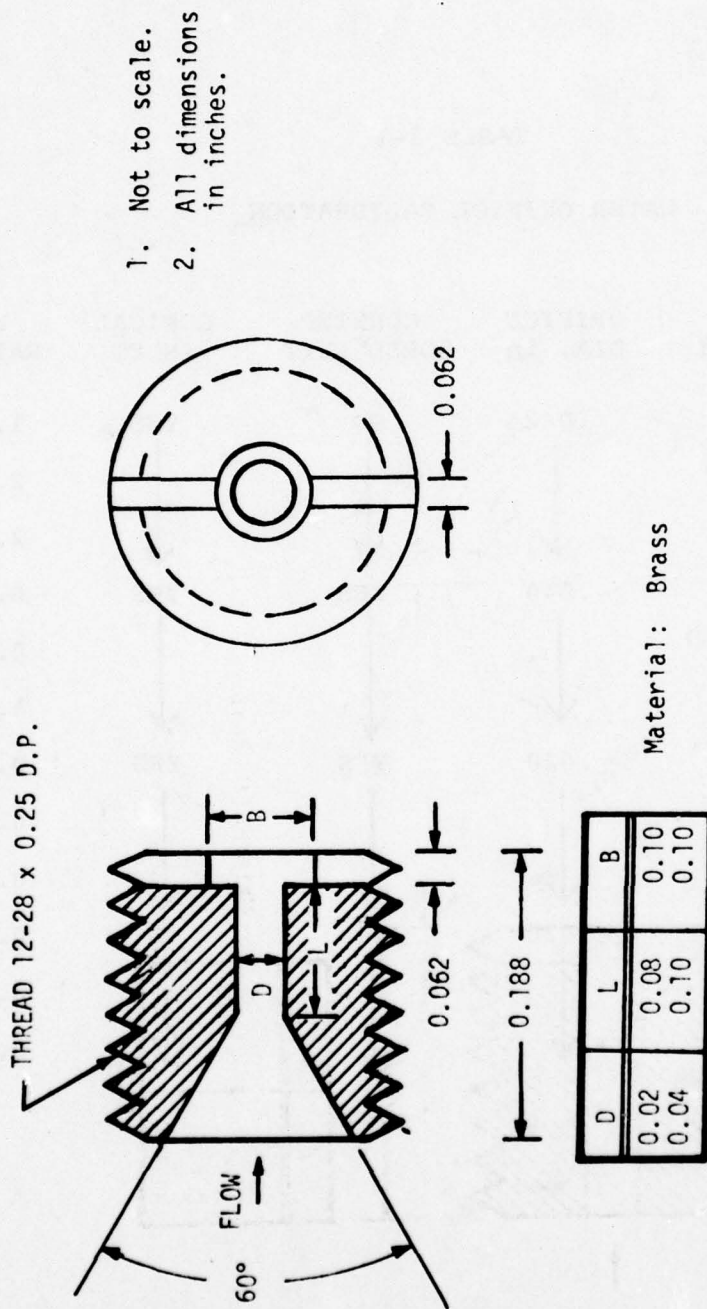
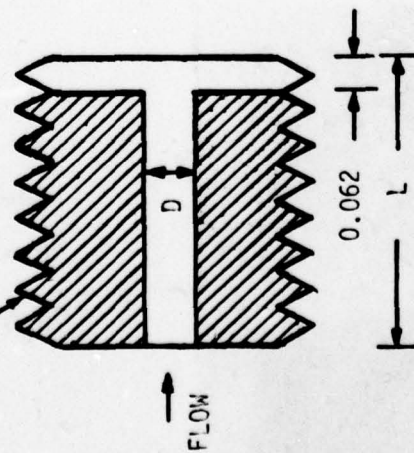


FIGURE 3-2. CONICAL INLET, COUNTERBORED EXIT DESIGN

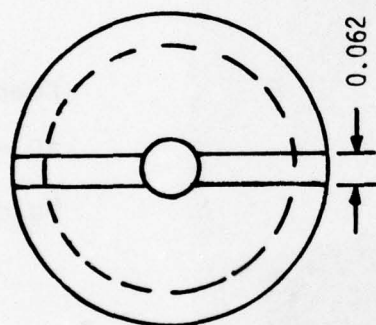


THREAD 12-28 x 0.25 D.P.



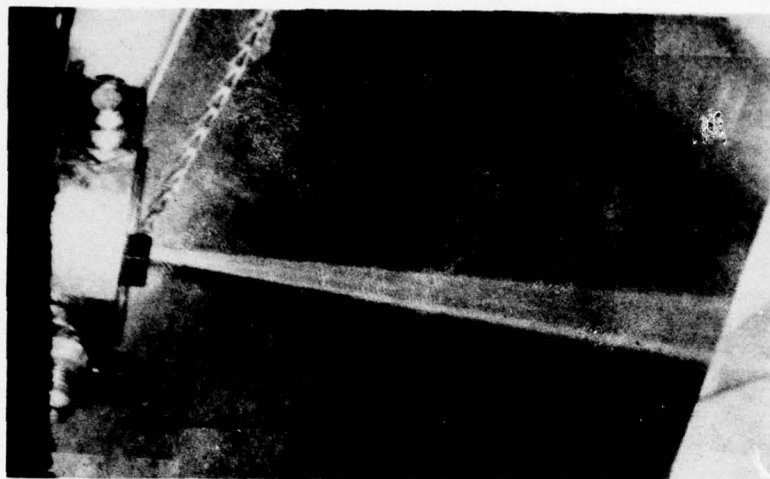
D	L
0.02	0.188
0.04	0.188
0.016	0.188
0.0625	0.188

Material: Brass



1. Not to scale.
2. All dimensions in inches.

FIGURE 3-3. STRAIGHT THROUGH DESIGN



Scene 1

$\Delta P = 200 \text{ psi}$

$\dot{M}_{H_2O} = 1.34 \text{ gal/min}$



Scene 2

$\Delta P = 500 \text{ psi}$

$\dot{M}_{H_2O} = 2.07 \text{ gal/min}$



Scene 3

$\Delta P = 800 \text{ psi}$

$\dot{M}_{H_2O} = 2.68 \text{ gal/min}$

FIGURE 3-4. WATER CALIBRATION FOR 0.062 IN. ORIFICE (SCENES 1-3)



Scene 4

$\Delta P = 200 \text{ psi}$

$\dot{M}_{H_2O} = 0.56 \text{ gal/min}$



Scene 5

$\Delta P = 500 \text{ psi}$

$\dot{M}_{H_2O} = 0.88 \text{ gal/min}$



Scene 6

$\Delta P = 800 \text{ psi}$

$\dot{M}_{H_2O} = 1.18 \text{ gal/min}$

FIGURE 3-5. WATER CALIBRATION TEST FOR 0.040 IN. ORIFICE (SCENES 4-6).





Scene 7

$\Delta P = 200 \text{ psi}$

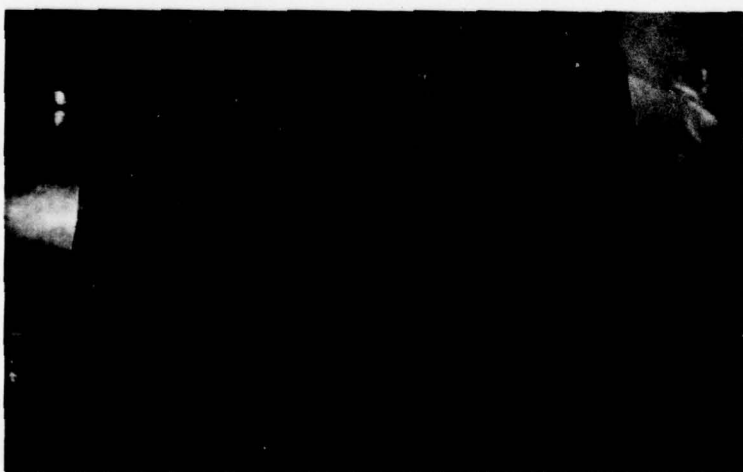
$\dot{M}_{H_2O} = 0.16 \text{ gal/min}$



Scene 8

$\Delta P = 500 \text{ psi}$

$\dot{M}_{H_2O} = 0.25 \text{ gal/min}$



Scene 9

$\Delta P = 800 \text{ psi}$

$\dot{M}_{H_2O} = 0.33 \text{ gal/min}$

FIGURE 3-6. WATER CALIBRATION TEST FOR 0.020 IN. ORIFICE (SCENES 7-9)



Scene 10

$\Delta P = 200 \text{ psi}$

$\dot{M}_{H_2O} = 0.15 \text{ gal/min}$



Scene 11

$\Delta P = 500 \text{ psi}$

$\dot{M}_{H_2O} = .22 \text{ gal/min}$



Scene 12

$\Delta P = 800 \text{ psi}$

$\dot{M}_{H_2O} = 0.28 \text{ gal/min}$

FIGURE 3-7. WATER CALIBRATION FOR 0.02 IN. ORIFICE  
(SCENES 10-12)

Figure 3-8 is the final calibration curve for each design. Also plotted are actual values for test runs. Differences apparently result due to a difference in exit orifice pressure from static throat pressure under dynamic flow conditions.

### 3.3.3 Models

The test models were 6Al-4V titanium consisting of eighteen 2.0 inch diameter (see Figure 3-9 for pre-test photos) and four 3.0 inch diameter models (see Figure 3-10 for pre-test photos). The hemispherical models all had a 0.25 inch skirt as shown in Figure 3-11 for attachment to the model holder shown in Figure 3-12. Each hemisphere was instrumented with eight platinum-platinum, 10 per cent rhodium thermocouples welded to the backside at the locations shown in Figure 3-11. Table 3-2 presents the pre-test skin thicknesses for each model and thermocouple location.

### 3.3.4 Instrumentation

In addition to the normal DET facility measurements, primary measurements on this program consisted of test section total pressure and total temperature, backface model temperatures, dust and water injection rates, water content in the test gas, and motion picture coverage.

A pressure probe was used to measure the pitot or normal shock recovery pressure. This probe was a hemisphere-cylinder with one inch diameter (Figure 3-13a) and a 1/16 inch diameter orifice at the sphere stagnation point. The total temperature probe, shown in Figure 3-13b, used a sheathed Pt-Pt, 13 per cent Rh thermocouple with a vapor-deposited junction shielded by a cylindrical tube made of magnesia-stabilized zirconia. The pressure probe and temperature probe outputs were recorded on conventional strip chart recorders. Model backside thermocouple outputs were



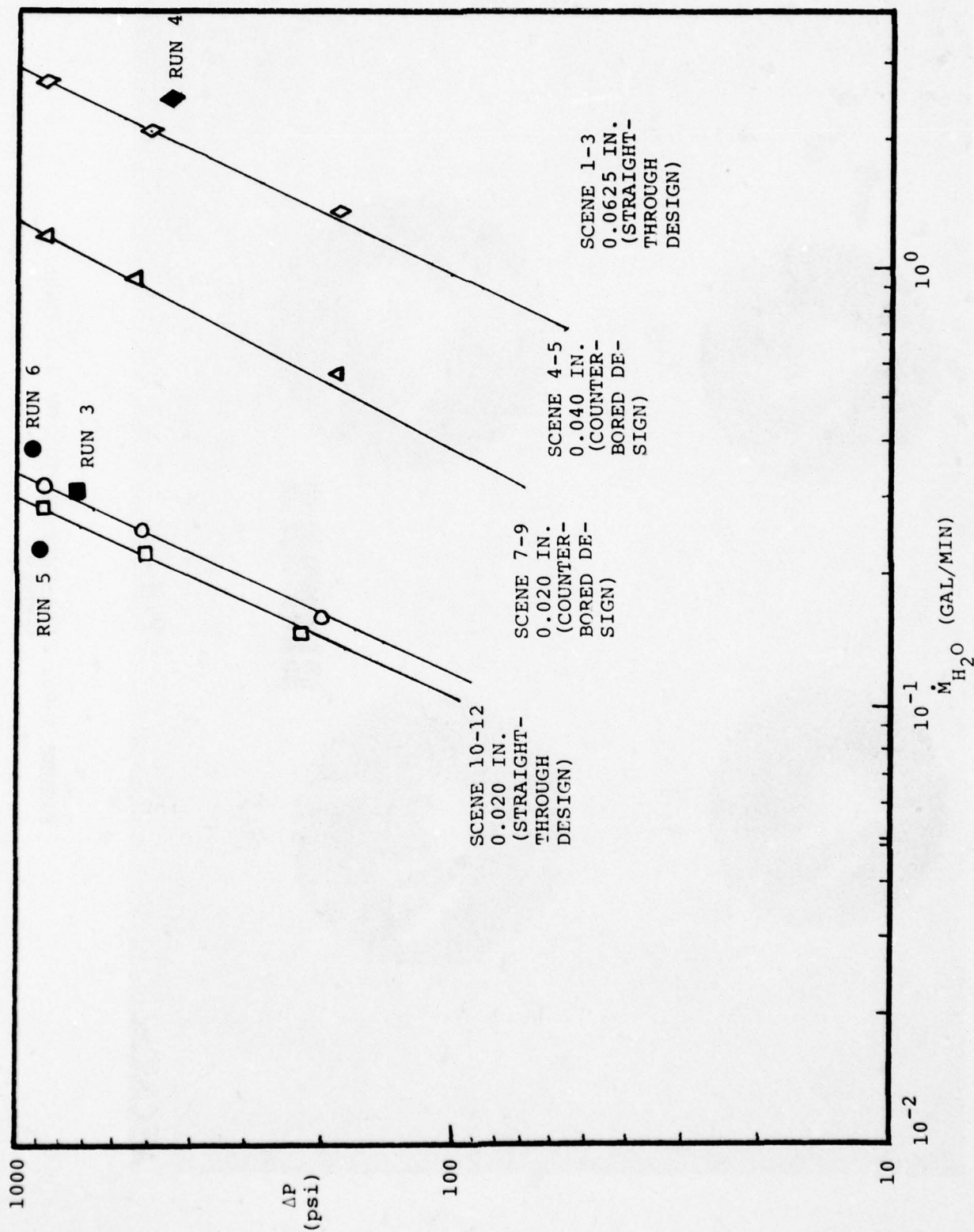


FIGURE 3-8. WATER ORIFICE CALIBRATION RESULTS

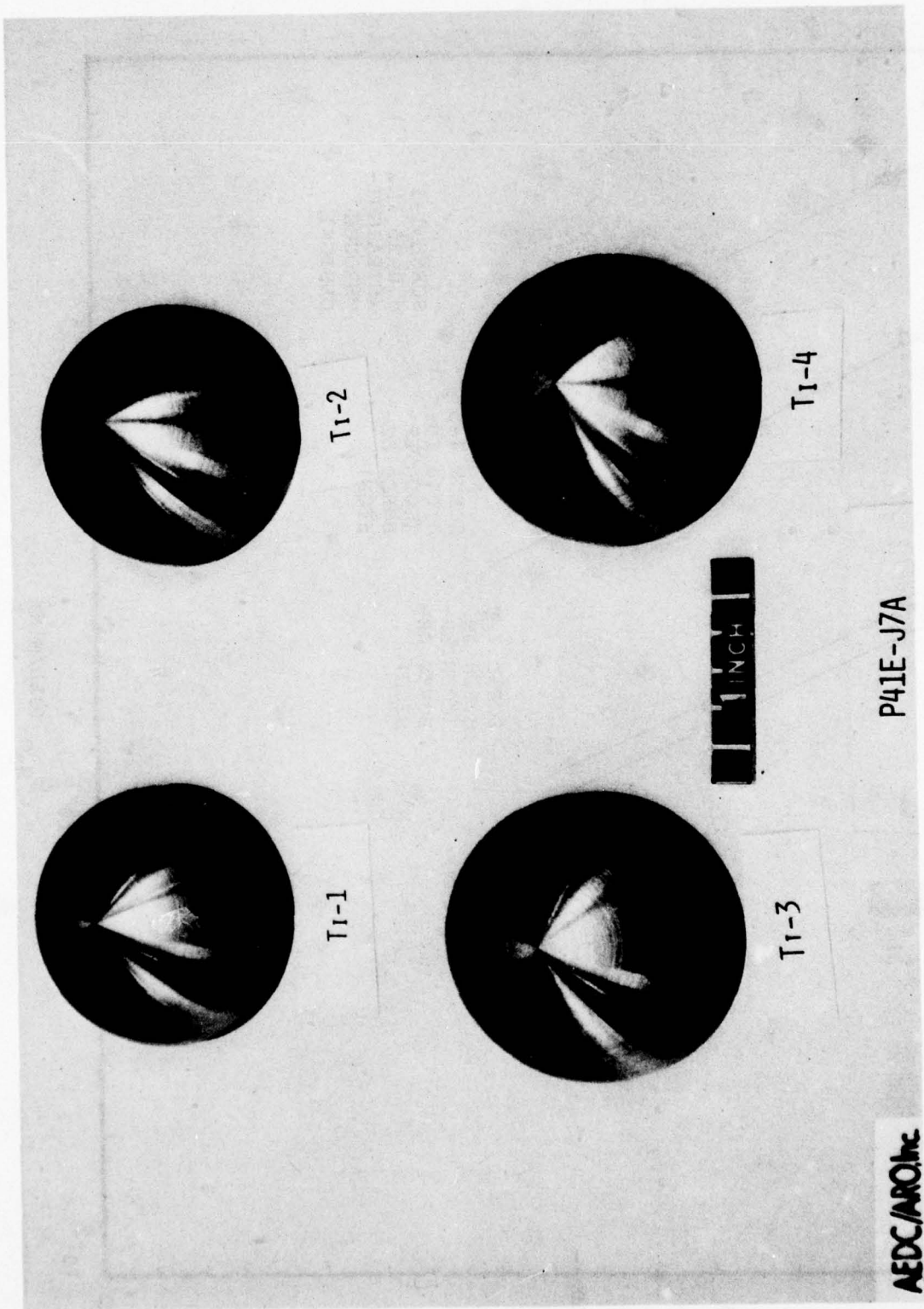


FIGURE 3-9a. PRE-TEST PHOTOS OF 2.0 INCH MODELS

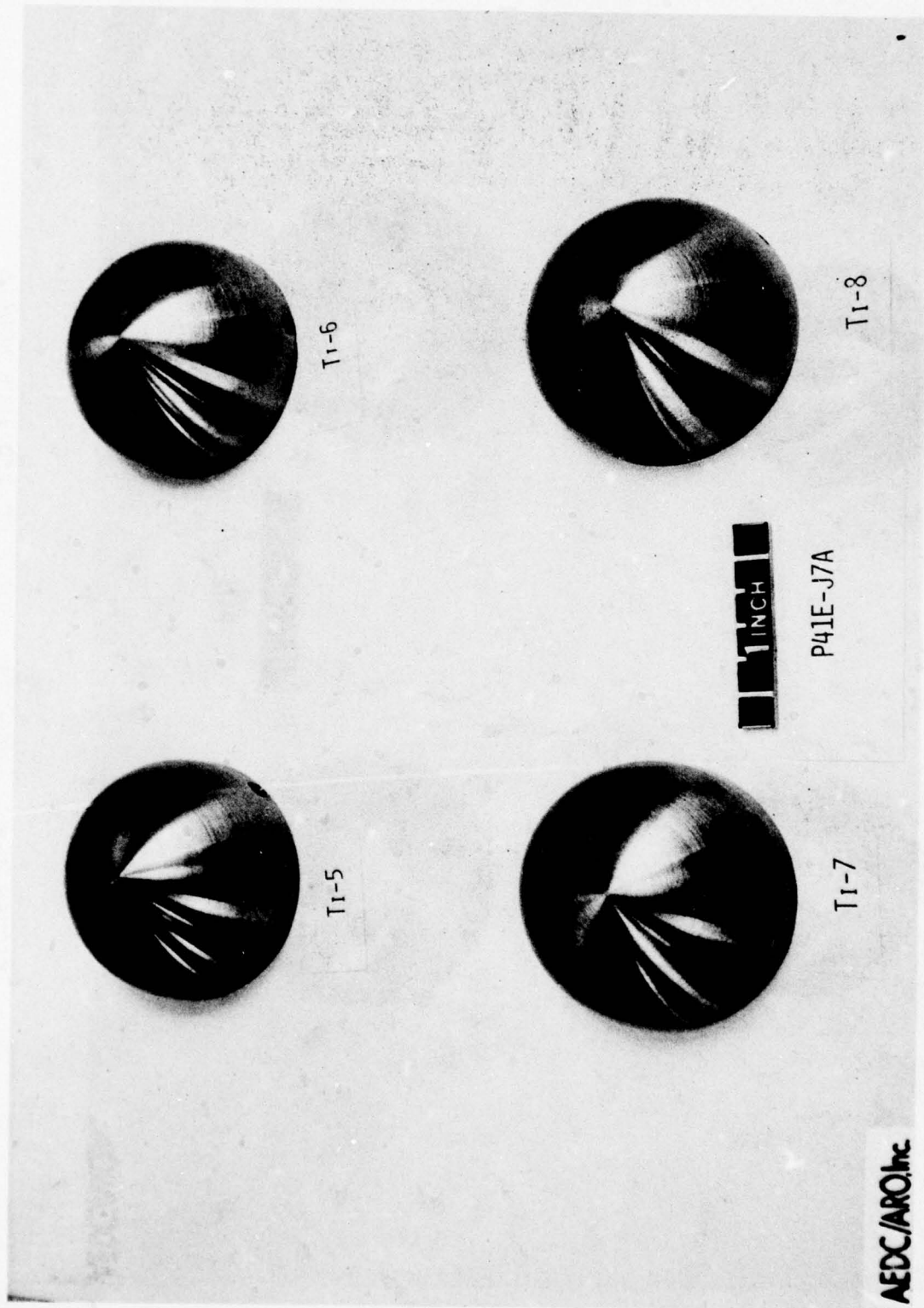


FIGURE 3-9b. PRE-TEST PHOTOS OF 2.0 INCH MODELS



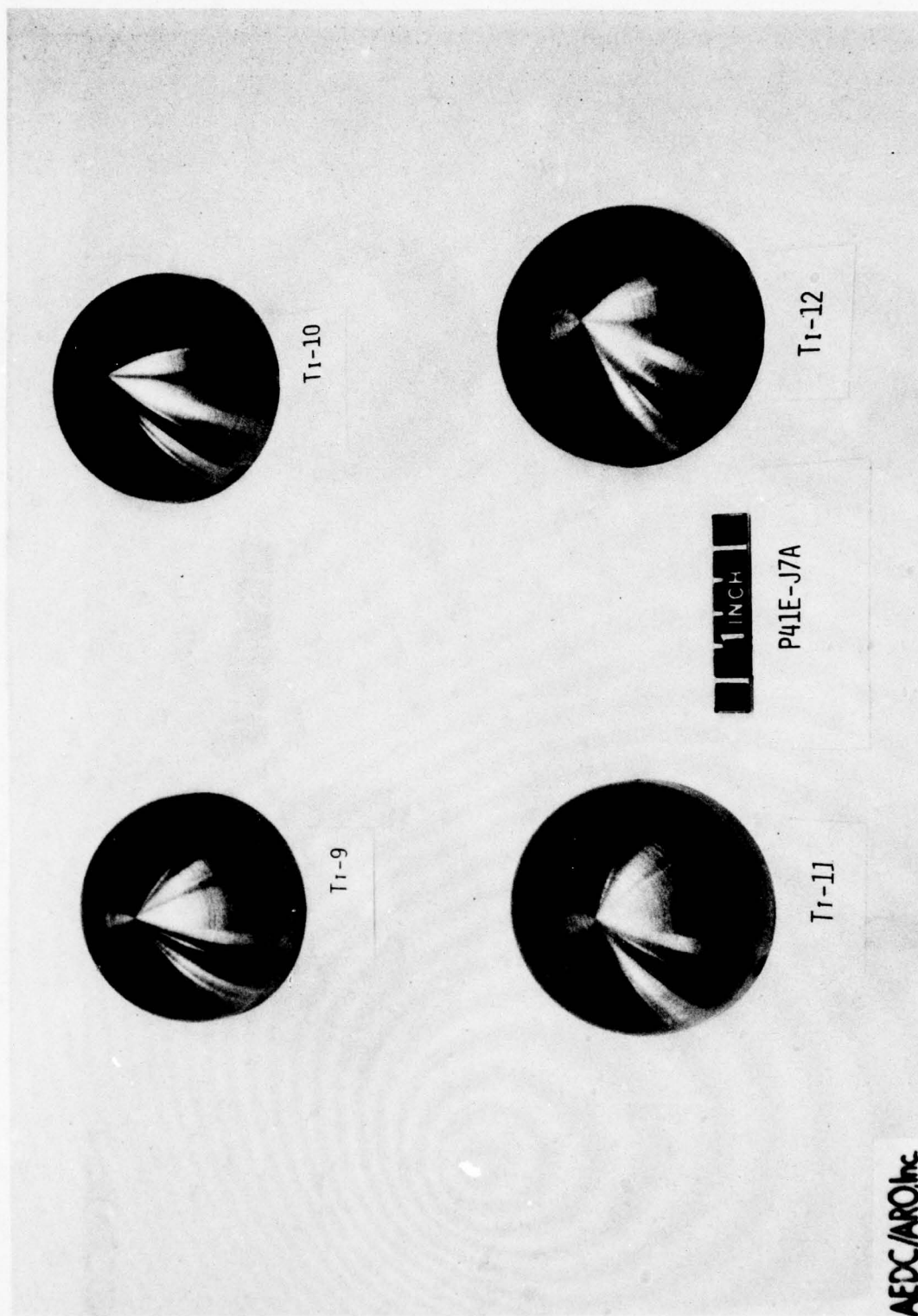


FIGURE 3-9c. PRE-TEST PHOTOS OF 2.0 INCH MODELS

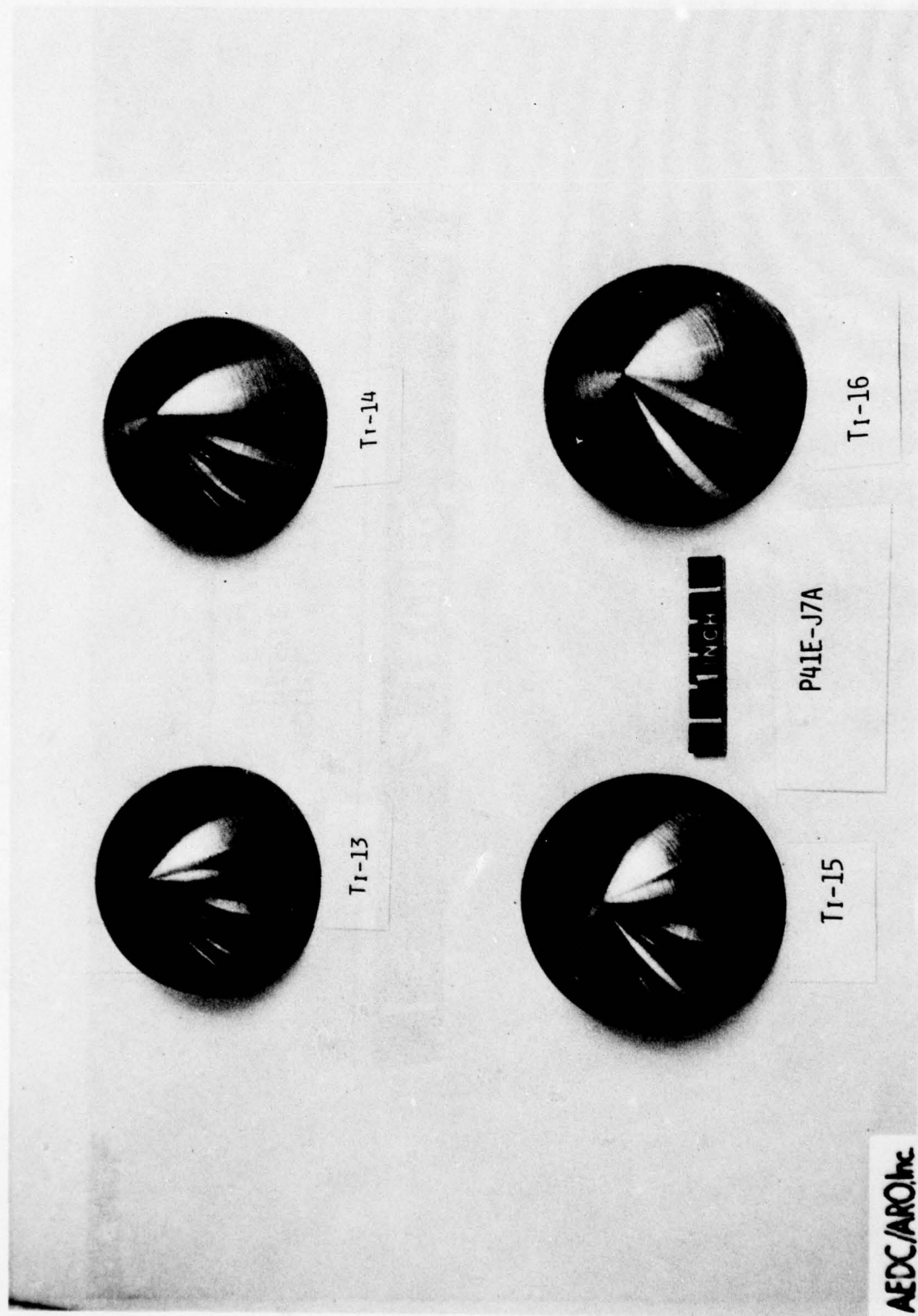


FIGURE 3-9d. PRE-TEST PHOTOS OF 2.0 INCH MODELS

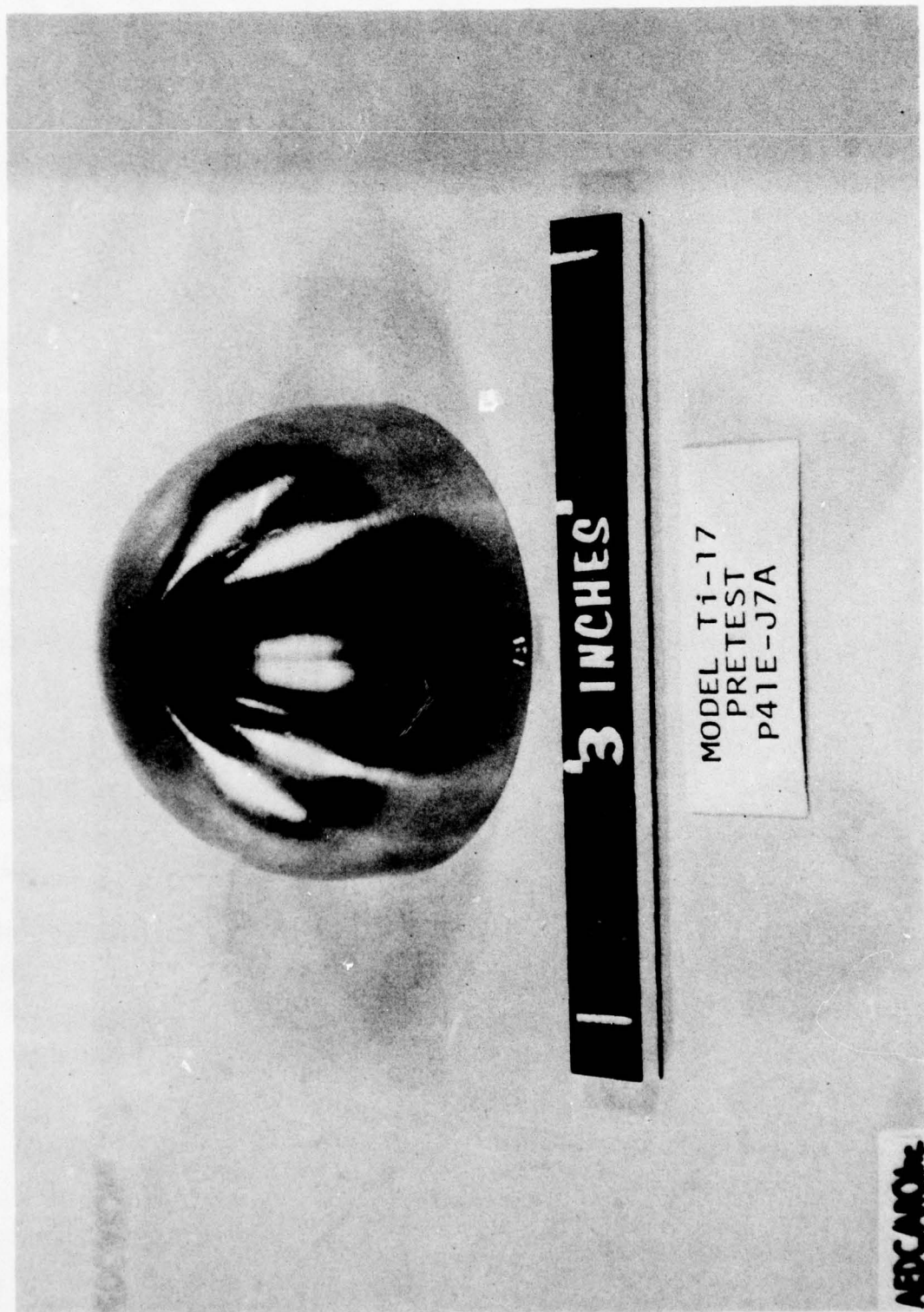


FIGURE 3-9e. PRE-TEST PHOTOS OF 2.0 INCH MODELS



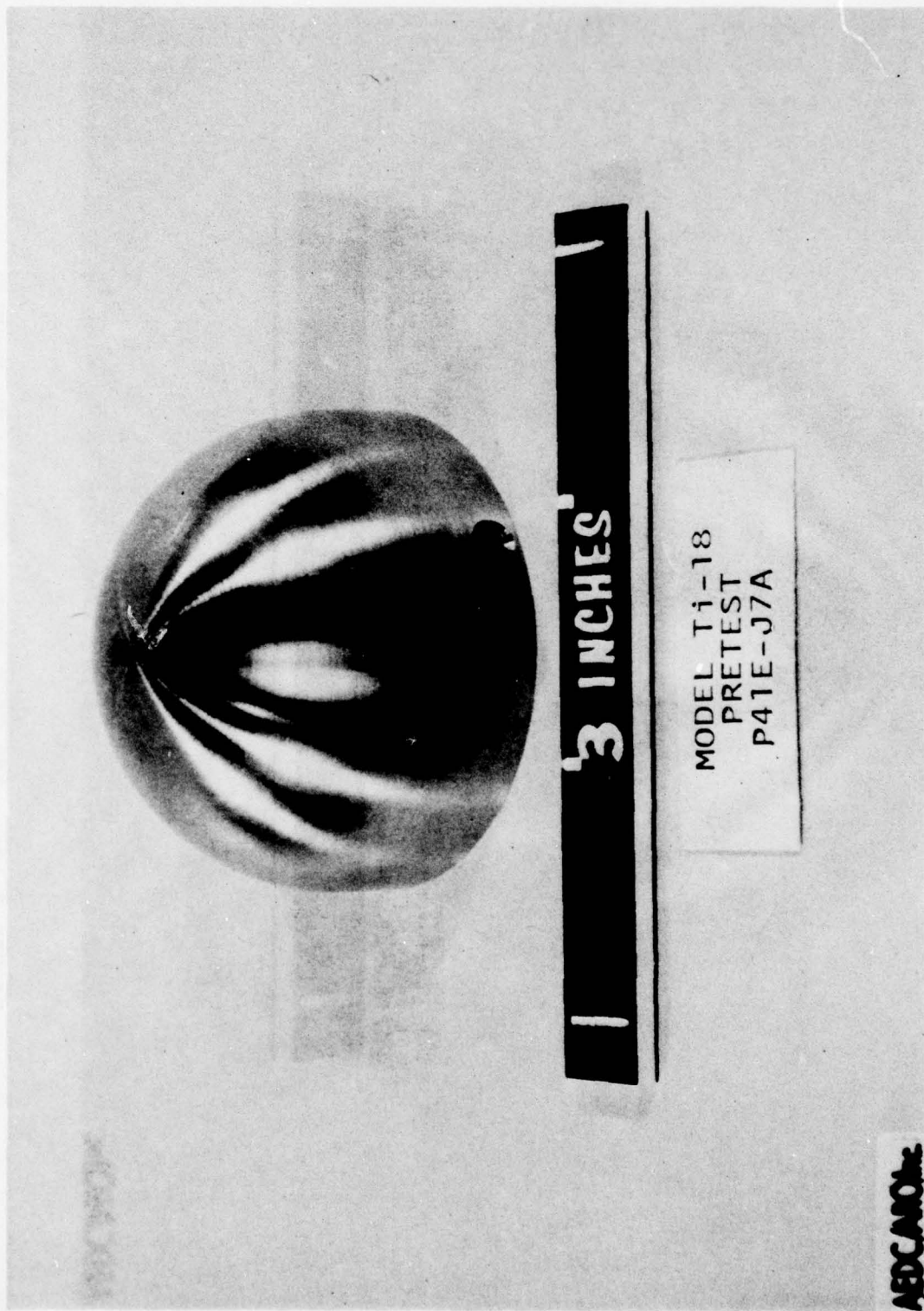


FIGURE 3-9f. PRE-TEST PHOTOS OF 2.0 INCH MODELS

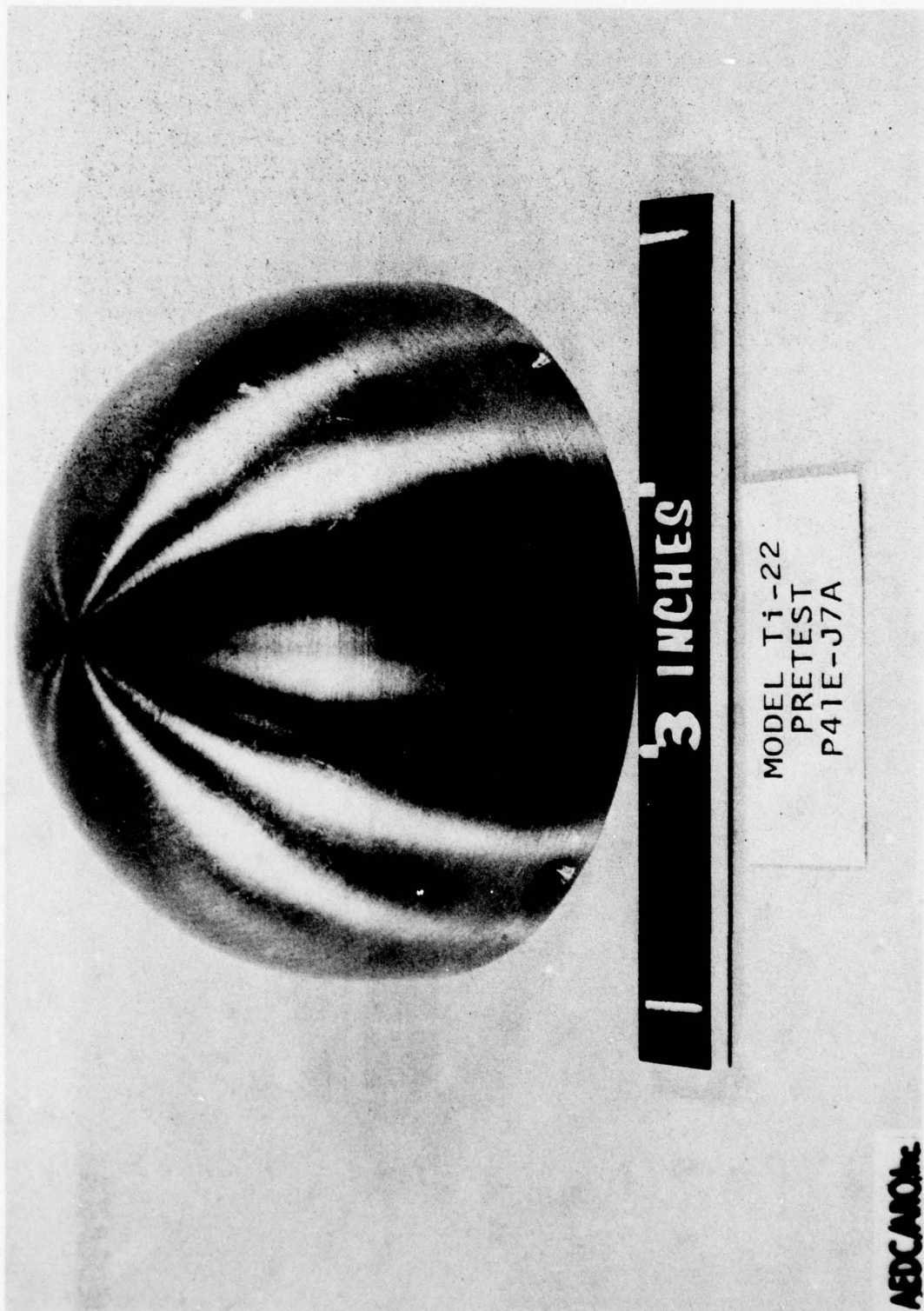


FIGURE 3-10a. PRE-TEST PHOTOS OF 3.0 INCH MODELS

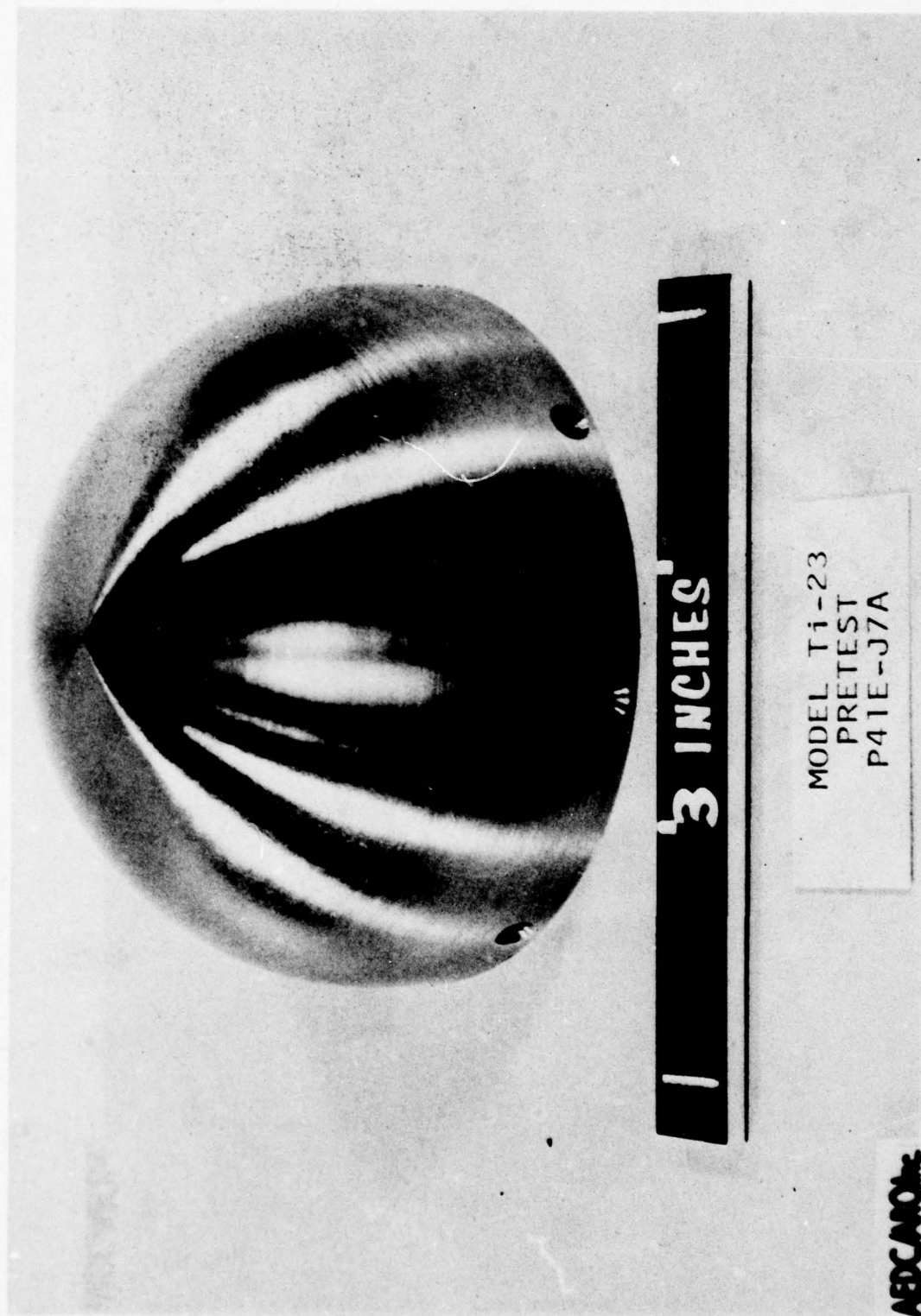


FIGURE 3-10b. PRE-TEST PHOTOS OF 3.0 INCH MODELS



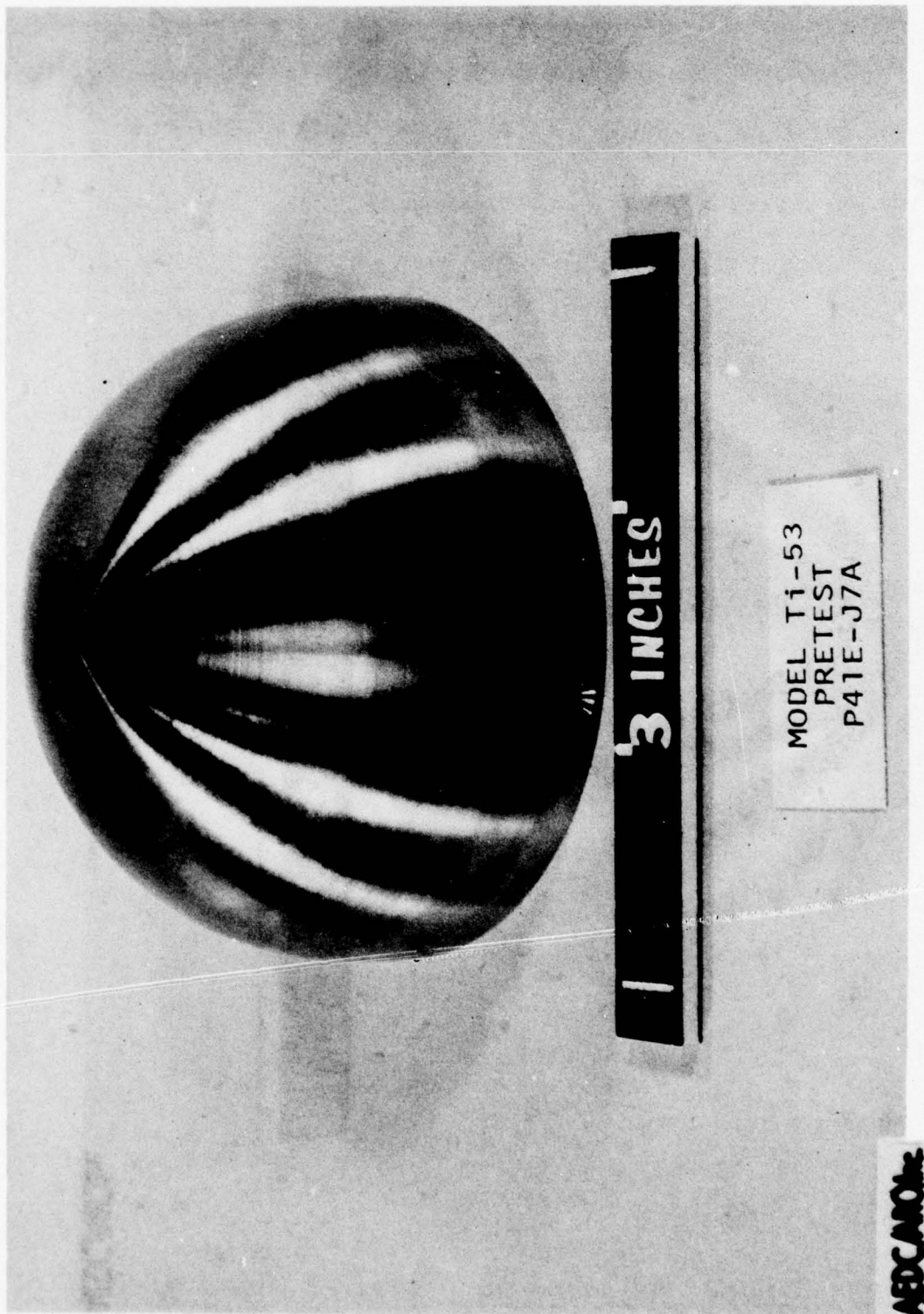


FIGURE 3-10c. PRE-TEST PHOTOS OF 3.0 INCH MODELS

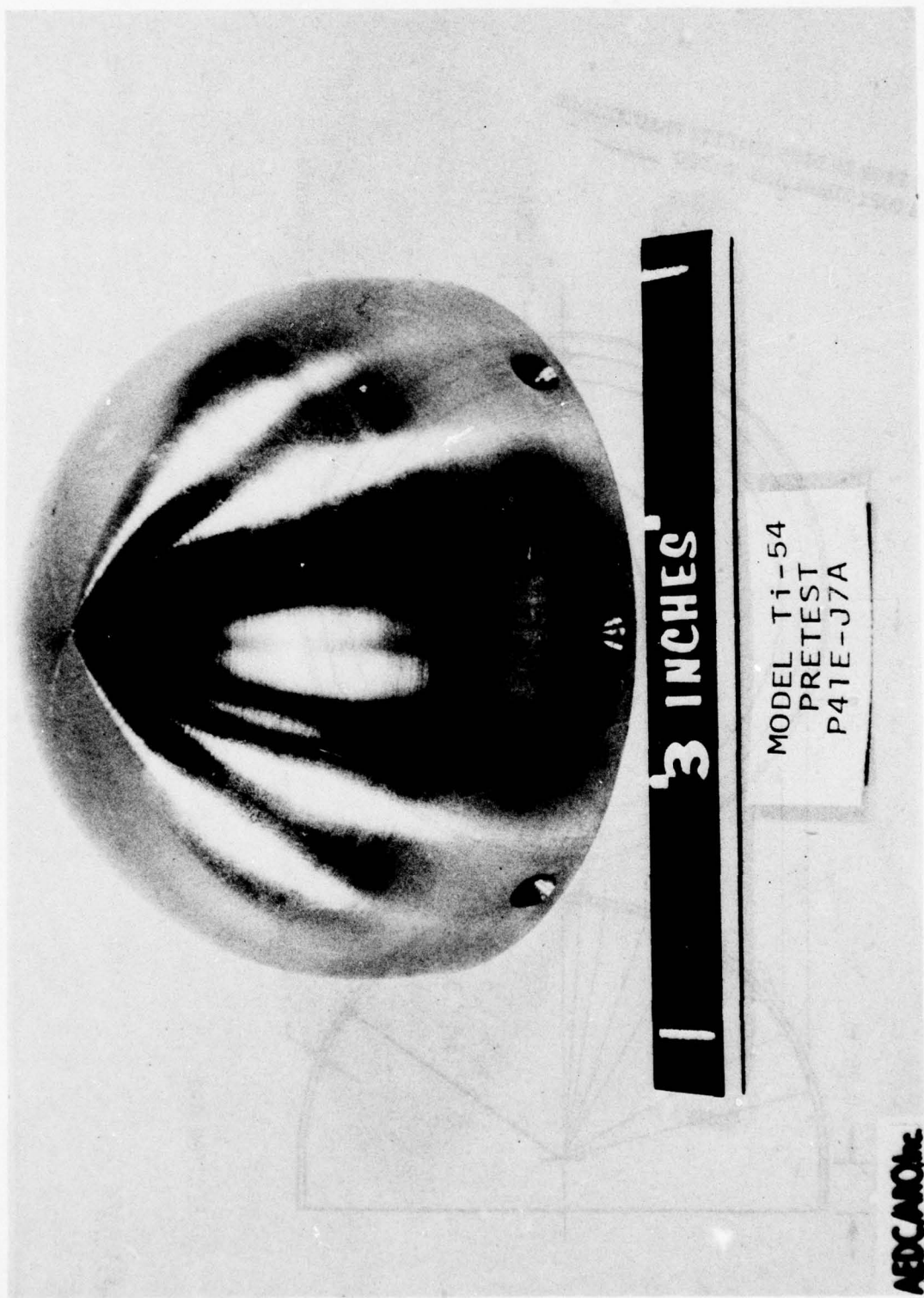


FIGURE 3-10d. PRE-TEST PHOTOS OF 3.0 INCH MODELS

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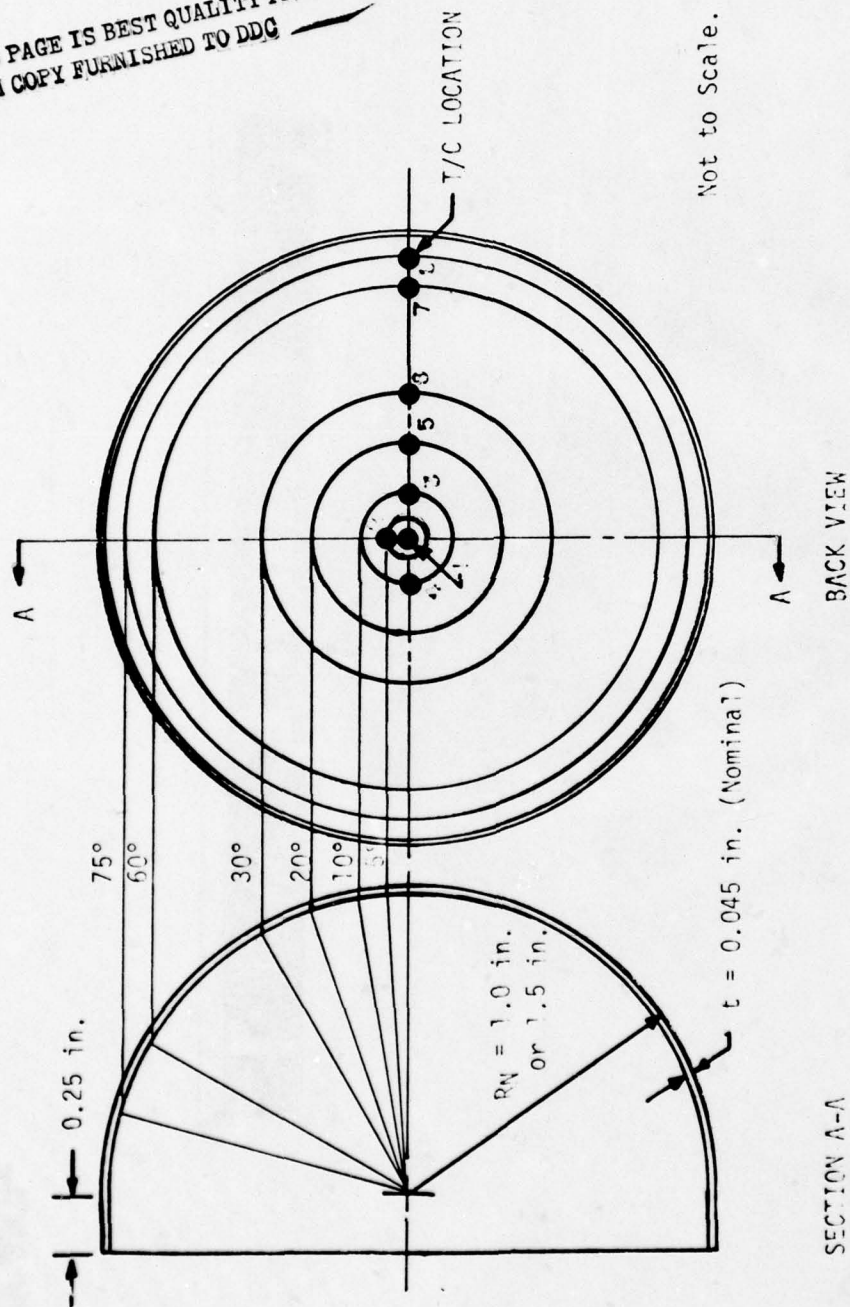


FIGURE 3-11. HEMISPHERE MODEL DESCRIPTION



TABLE 3-2. PRE-TEST TITANIUM HEMISPHERE THICKNESSES (INCHES)

MODEL NO.	LOCATION ON MODEL (POSITION/ANGLE)							
	1 0°	2 5°	3 10°	4 10°	5 20°	6 30°	7 60°	8 75°
Ti-1	.051	.049	.047	.047	.045	.042	.037	.036
Ti-2	.046	.045	.043	.043	.042	.037	.035	.035
Ti-3	.047	.045	.045	.044	.043	.042	.037	.037
Ti-4	.050	.048	.047	.047	.045	.042	.036	.035
Ti-5	.041	.039	.038	.037	.038	.036	.036	.037
Ti-6	.043	.042	.040	.039	.039	.038	.035	.038
Ti-7	.050	.048	.047	.048	.046	.044	.041	.041
Ti-8	.052	.051	.049	.049	.048	.044	.040	.037
Ti-9	.033	.032	.031	.032	.030	.031	.033	.037
Ti-10	.046	.044	.043	.043	.043	.038	.036	.035
Ti-11	.042	.040	.038	.038	.039	.037	.036	.036
Ti-12	.044	.042	.041	.041	.040	.038	.032	.033
Ti-13	.043	.040	.040	.038	.039	.037	.035	.036
Ti-14	.049	.047	.045	.046	.044	.040	.038	.037
Ti-15	.049	.047	.045	.046	.045	.042	.037	.037
Ti-16	.046	.044	.045	.045	.045	.046	.047	.047
Ti-17	.049	.049	.048	.047	.050	.046	.038	.036
Ti-18	.050	.049	.049	.048	.050	.046	.038	.037
Ti-22	.039	.038	.038	.039	.038	.034	.039	.042
Ti-23	.047	.044	.044	.043	.042	.042	.045	.048
Ti-53	.079	.078	.080	.079	.083	.082	.081	.075
Ti-54	.065	.066	.067	.066	.068	.070	.076	.079

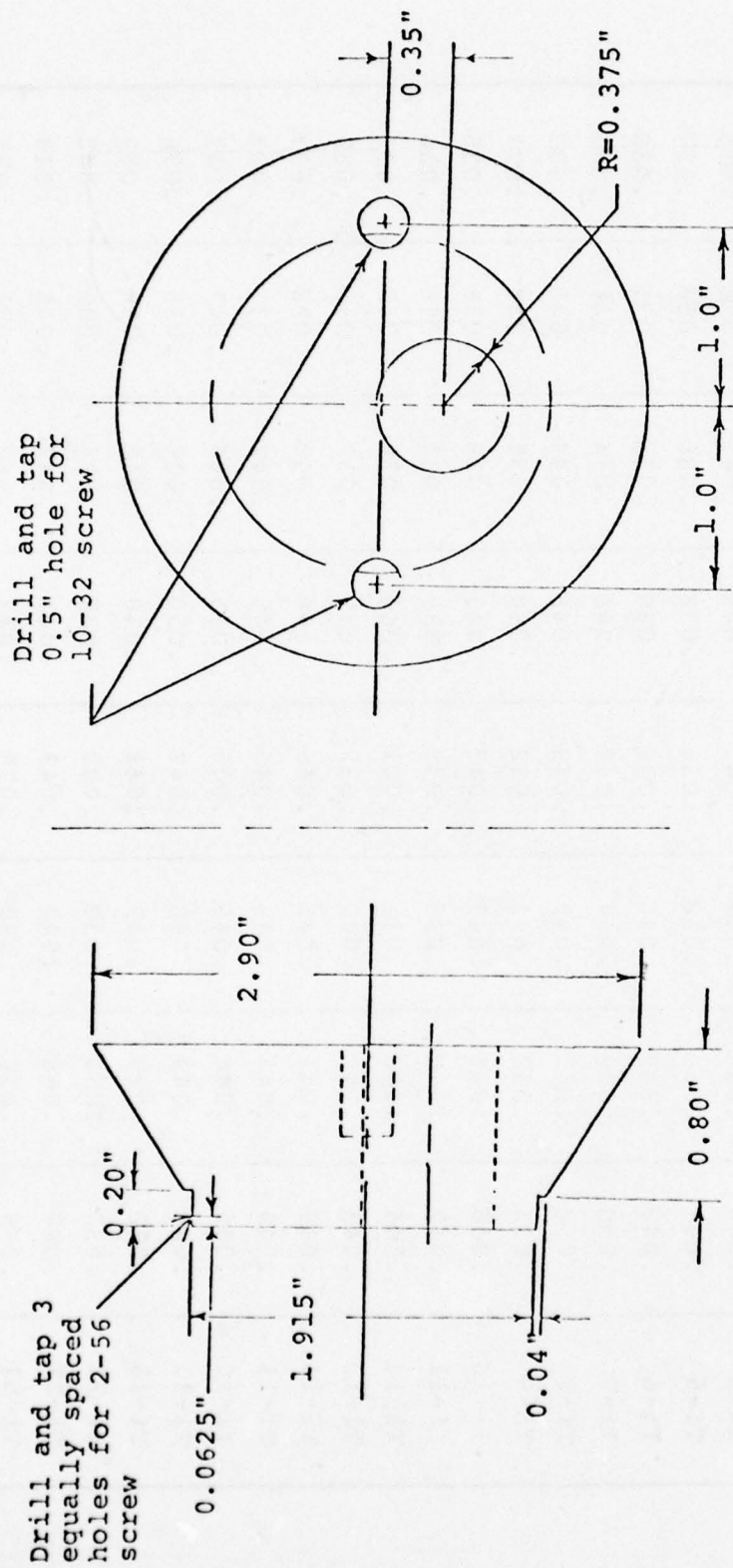
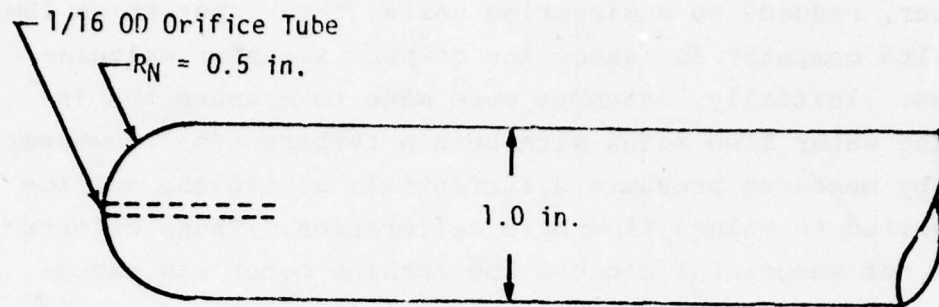
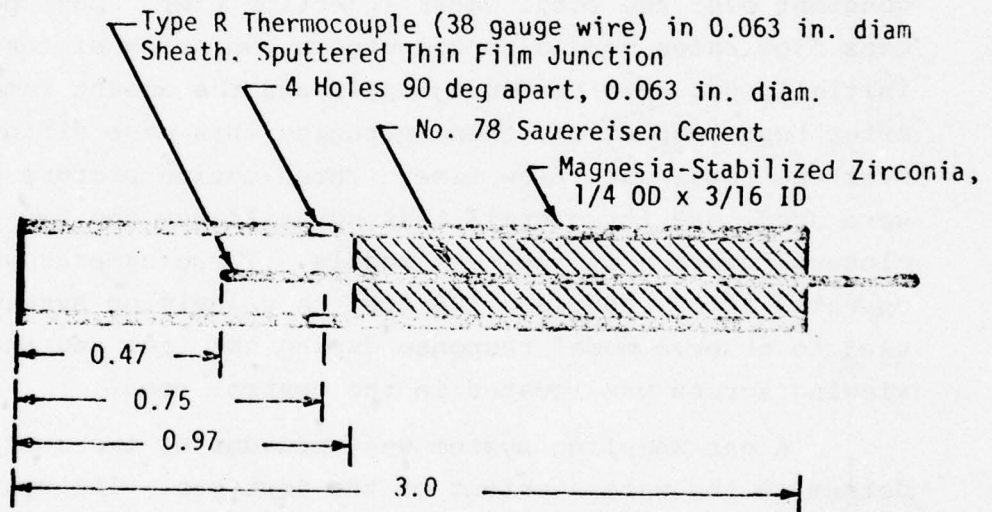


FIGURE 3-12. SKETCH OF MODEL HOLDER FOR THOSE MODELS USING SPOT WELDED THERMOCOUPLES



a. Pressure Probe



Not to Scale - All dimensions in inches.

b. Temperature Probe

FIGURE 3-13A&B. PRESSURE AND TEMPERATURE PROBES



recorded on magnetic tape using an analog-to-digital converter, reduced to engineering units, then input to an IBM 370/165 computer for execution of heat transfer calculations. Initially, attempts were made to measure the injected water flow rates with both a turbine-type flowmeter and by measured pressure differentials across the orifice converted to volume flow by a calibration. These efforts were not successful because the turbine meter was exceptionally susceptible in electrical noise pickup from the arc heater and the  $\Delta P$  calibrations could not be performed under the same conditions as the orifices were subjected to during a test run. Beginning with Run 3, the water was weighed before and after the test run and the flow rate was assumed constant over the total water injection time. Dust particle mass flow rates were also computed by weighing of the dust initially put into the dust hopper and the amount remaining after test completion, then averaging this mass difference over the total dust flow time. Three motion picture cameras were used, one for overall test surveillance and two for closeup coverage of the test models. These cameras were operated at 50, 200, and 400 fps. A television system was used to observe model response during the test and the viewing screen was located in the control room.

A gas sampling system was used during two runs to determine the water content of the test gas. The system consisted of a 2 inch diameter stainless steel hemisphere with a 1/16 inch diameter sampling orifice at the stagnation point, two stainless steel bottles of 300 cc capacity each, and several valves and connecting stainless steel tubing (see Figure 3-14). The bottles were evacuated and dried prior to the tests. During operation, the sampling line from the model was purged, then the remotely operated valves were opened for about 10 seconds each. The remotely actuated



FIGURE 3-14. GAS SAMPLER MODEL

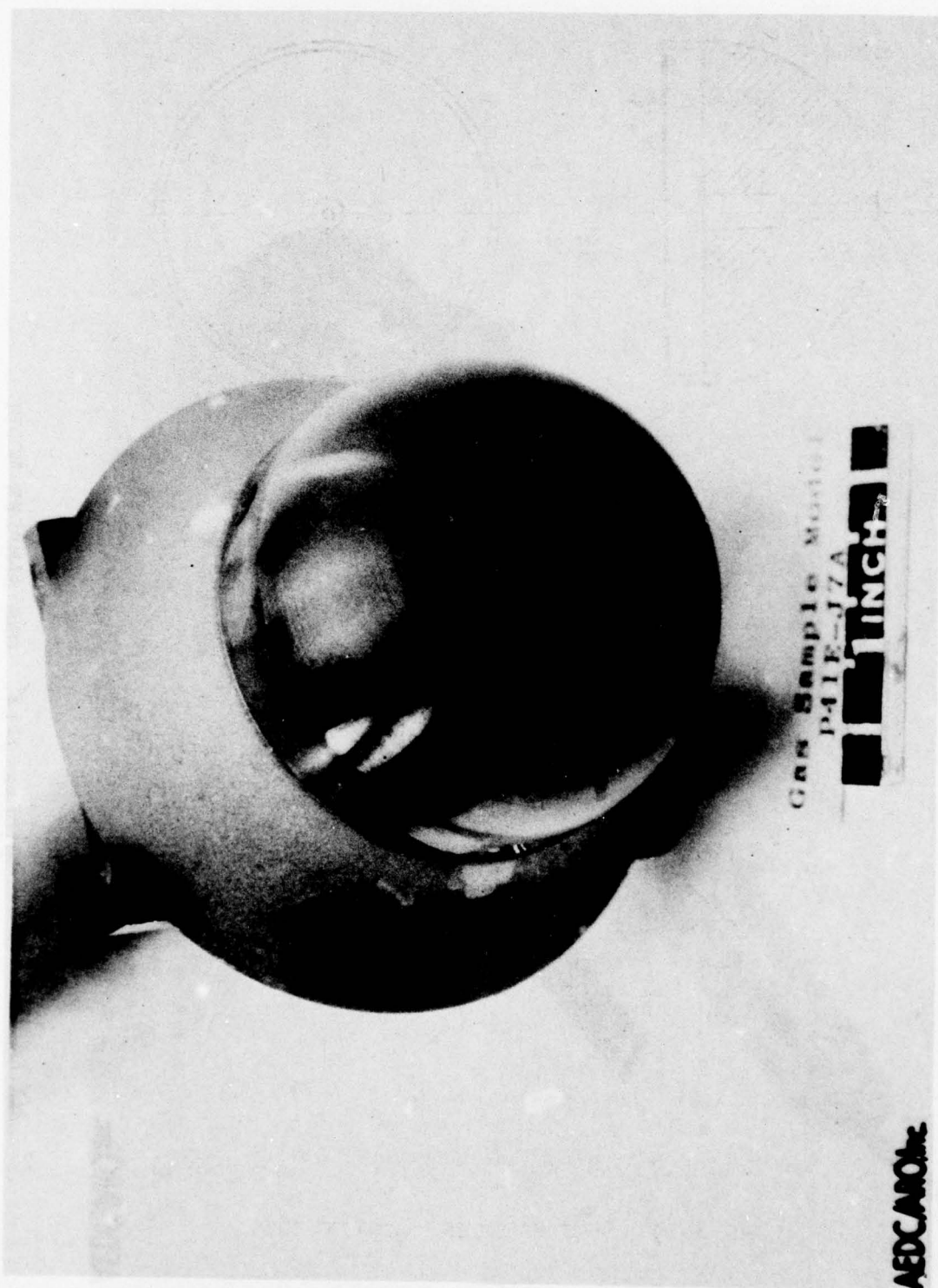


FIGURE 3-14. GAS SAMPLER MODEL (CONTINUED)



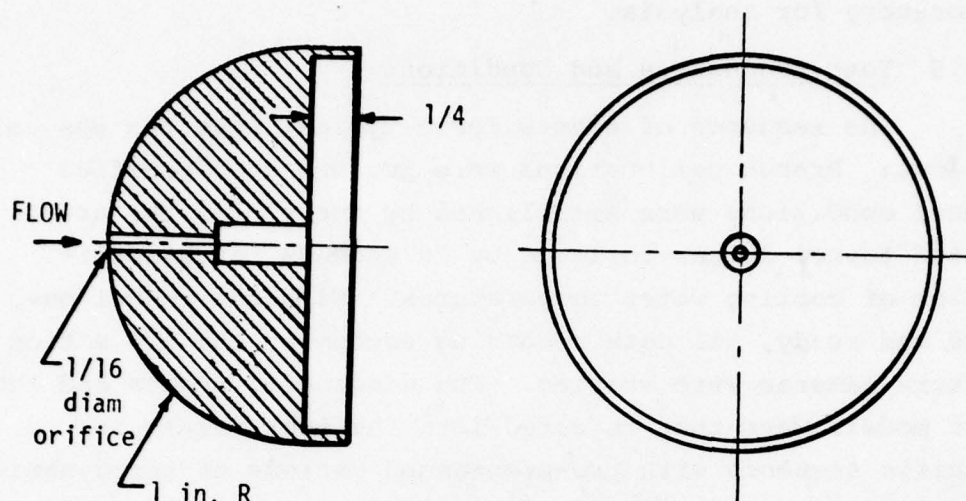
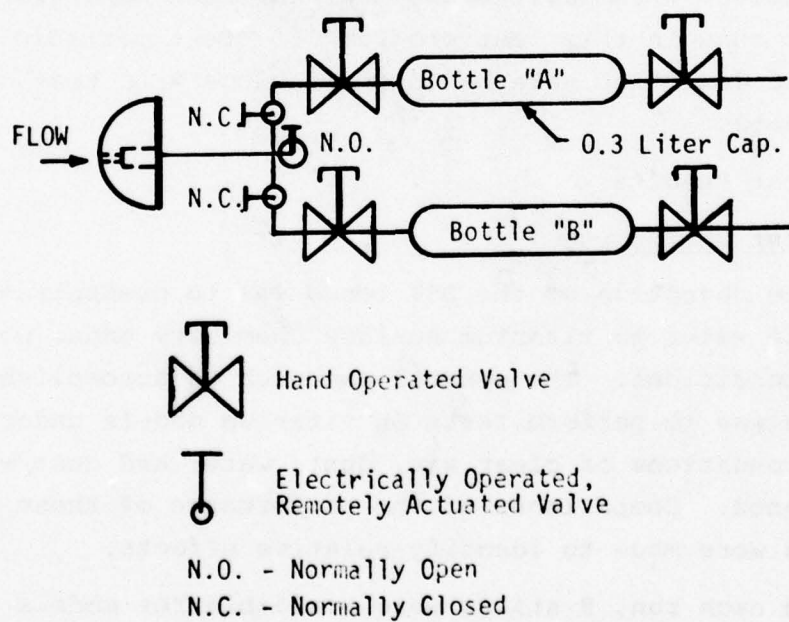


FIGURE 3-14. GAS SAMPLER (CONTINUED)



b. Schematic of Gas Sampling System

FIGURE 3-14. GAS SAMPLER (CONTINUED)

valves were then closed, and after the test run, the hand valves were closed and the bottles sent to the AEDC Chemical Laboratory for analysis.

### 3.3.5 Test Procedures and Conditions

The sequence of events for a typical test run was as follows: Prerun calibrations were performed. Specified tunnel conditions were established by energizing the arc-heated tunnel driver followed by 20 seconds for stabilization of cooling water temperatures. With the tunnel on-line and ready, all data recording equipment and all motion picture cameras were started. The diagnostic probes and the test models were then injected into the test stream in specific sequence with pre-programmed periods of aerodynamic heating and/or dust and water exposure. After all models had been cycled through the flow, the tunnel driver was de-energized; then the postrun calibrations were performed.

Table 3-3 summarizes the AEDC DET test conditions for the eight runs in this test program<sup>(7)</sup>. Dust particle velocities and densities were based on previous AEDC test calibration data.

## 3.4 Test Results

### 3.4.1 Test Philosophy

The objective of the DET tests was to demonstrate the effects of water on titanium surface chemistry under particle erosion conditions. The general approach to accomplish this objective was to perform tests on titanium models under varying conditions of clear air, dust, water and dust/water environments. Comparisons of the performance of these model responses were made to identify relative effects.

In each run, 9 stings were available for models or instrumentation. Typically, these stings were occupied by one pressure probe, one temperature probe, four models, and

TABLE 3-3. AEDC DET TEST CONDITIONS

RUN NO.	NO.	MODELS	RN (IN)	P <sub>0</sub> (PSIA)	P <sub>stag</sub> (PSIA)	H <sub>0</sub> (BTU/LB)	T <sub>STAG</sub> (°F)	$\dot{M}_{AIR}$ (LB/SEC)	$\dot{M}_{H_2O}$ (LB/SEC)	$\rho_{DUST}$ (10 <sup>-8</sup> g/cc)	V <sub>DUST</sub> <sup>†</sup> (FT/SEC)	$\dot{e}_{DUST}$ <sup>†</sup> (BTU/FT <sup>2</sup> -SEC)	GAS SAMPLER $\Delta M_{H_2O}$ (mg) $\Delta M_{AIR}$ (mg) $\Delta t$ (SEC)
1													
2	4		1.0	994	10	765	2430	2.9	.02	34	4600	41	--
3	4		1.0	1055	10	580	1809*	3.7	.04	45	4200	42	--
4	4		1.0	530	5.3	550	1702*	1.9	.35	34	4130	30	--
5	4		1.0	500	5.3	515	1568*	2.0	.04	39	4030	32	.76 116 25
6	4		1.0	994	9.4	780	2464*	2.7	.065	23	4560	27	4.0 194 20+
7	4		1.5	1002	9.8	1806	5440	1.7	.058	27	5530	57	--
8	4		1.0	1004	9.9	1865	5560	1.7	.048	18	5560	38	--

..... CALIBRATION .....

MODIFIED NOZZLE, STATION 127.5 INCHES, FOR ALL RUNS

\* Temperature probe, all others based on mass-average enthalpy

† 100  $\mu$  M.O



witness bars or empty stings. For the high enthalpy runs, no temperature probe was used since it would not survive. In several runs, the gas sampler was used to measure water content in the test gas.

Primary data was the model backface temperature response. Attention was focused on the stagnation region response. Comparisons of this temperature data and reduced heat transfer data for the stagnation point were used to determine the effect of water on the titanium response.

This test program encountered a number of problems in the initial stages of testing related to facility calibration and operation which were ultimately corrected. Part of the difficulties were associated with the injection of water which had never been attempted previously. It was especially difficult to positively confirm the presence and state of the water at the test section. Witness bars, motion picture coverage, and ultimately the gas sampler instrument were used to confirm the presence and/or amounts of water at the test section. Originally, four runs were planned with a required expansion to eight runs to accomplish the objectives of the program.

The detailed test data results for Runs 2-8 are presented in Appendix A. Run 1 was for calibration purposes and is not discussed in this report. The basic data shown in Appendix A includes: (1) post-test model photographs; (2) total temperature probe trace (if available); (3) model backface temperature measurements for all thermocouple locations; and, (4) reduced heat transfer data for all thermocouple locations. A discussion of the stagnation point results of Runs 2-8 is presented in the following section.

#### 3.4.2 Discussion of AEDC DET Runs

Figures 3-15 - 3-21 present the results of AEDC DET Runs 2-8. The backface stagnation point thermocouple temperature-time response and reduced heat transfer are shown for

each of the models tested. Runs 2-6 models were 2-inch diameter and Runs 7-8 models were 3-inch diameter titanium (6Al-4V) hemispheres of varying skin thicknesses -- model numbers and stagnation point skin thicknesses are noted on the figures. Test conditions including the dust and water environments are shown. In most cases, stagnation pressure and temperature were measured with probes except for Run 2, where the temperature probe did not operate correctly and the reported value is based on an energy balance and Runs 7 and 8 which were high enthalpy where the probe would not survive.

Figures 3-15 and 3-16 show the results for the initial Run 2 with nominal flow conditions of 1000 psia total pressure and 800 Btu/lb total enthalpy and a low water injection rate. These results show the expected clear air and dust response including the high temperature ( $>2200^{\circ}\text{R}$ ) chemistry effect based on previous studies (Reference 4). No increased effect of water is shown. The higher temperatures for the dust/water model Ti-6 compared to the dust model Ti-1 result from a thinner skin only. In fact, no effect of water, even a cooling effect, is shown. Figure 3-16 shows the reduced heat transfer rate at the stagnation point. This reduced data is characterized by: (1) an initial transient increase to the  $\sim 1000$ - $1500^{\circ}\text{R}$  regime; (2) a decreasing heat transfer with increasing temperature characteristic of a convective heating trend in the  $\sim 1500$ - $2000^{\circ}\text{R}$  regime; (3) an increasing heat transfer with increasing temperature in the  $>2200^{\circ}\text{R}$  regime characteristic of a dominating surface chemistry effect; and, (4) periodic erratic behavior due to electrical noise in the thermocouple output. Typically,  $2000^{\circ}\text{R}$  is an excellent temperature to compare relative heat transfer. Figure 3-16 shows no increased effect of water and, in fact, possibly a reduced heat transfer for the dust and water model. This run did not have the

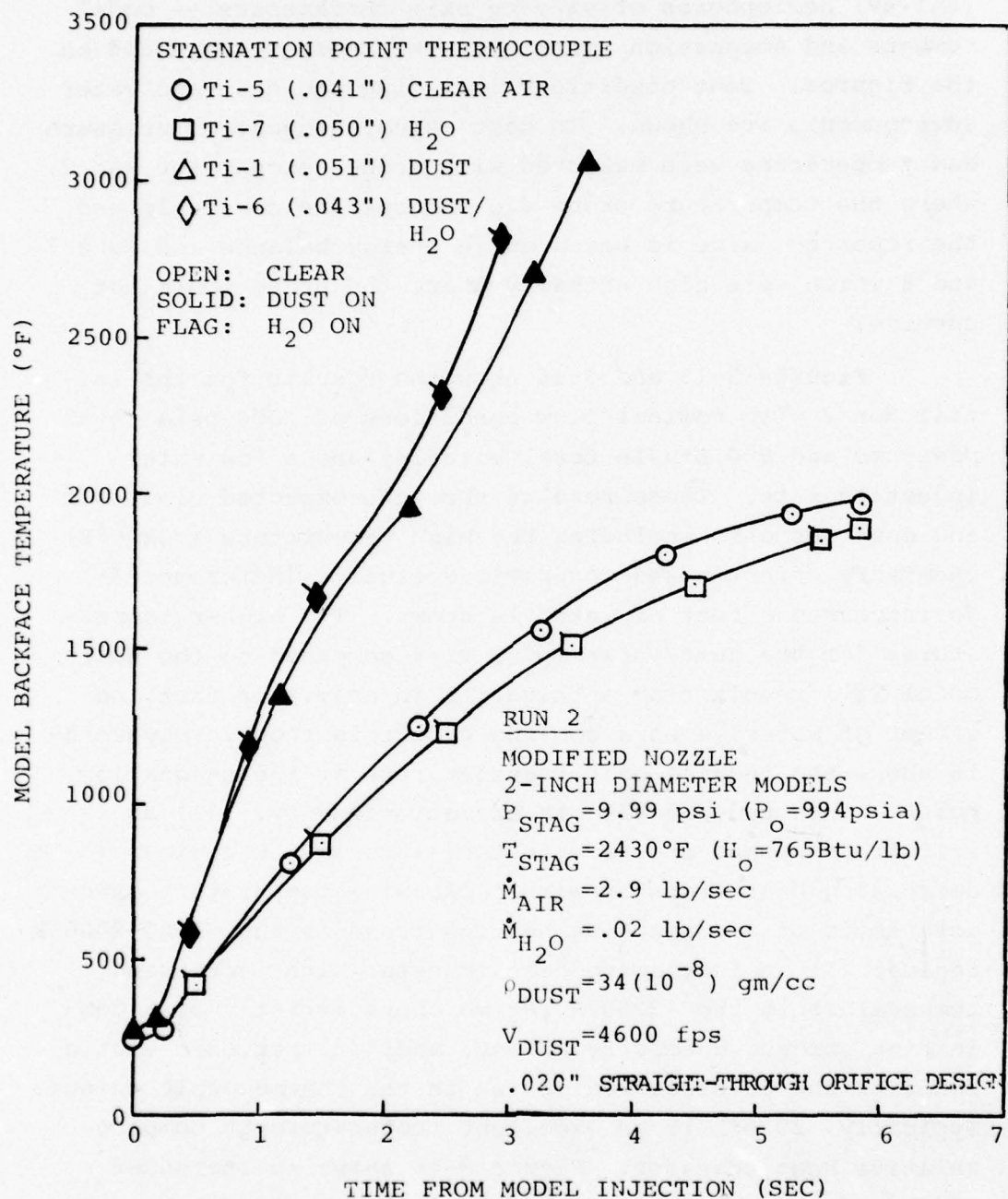
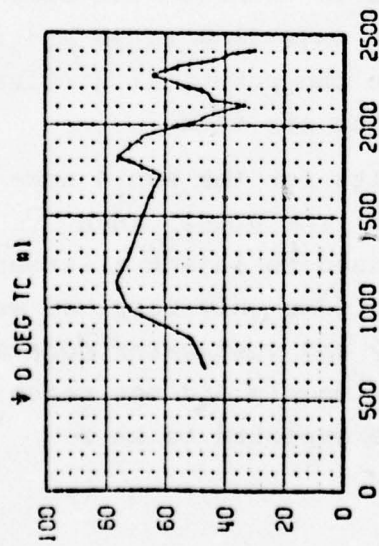


FIGURE 3-15. STAGNATION POINT RESULTS FOR AEDC DET RUN 2



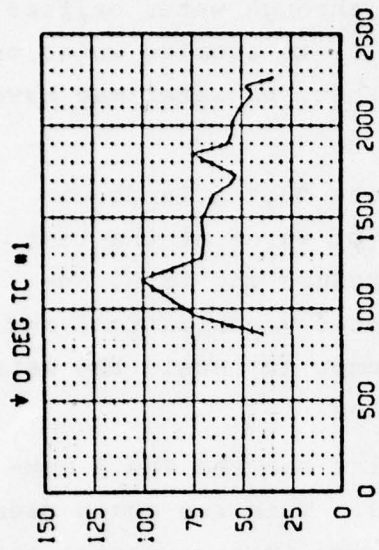
MODEL TI-5 CLEAR

Time = 16.06 to 22.60 Sec



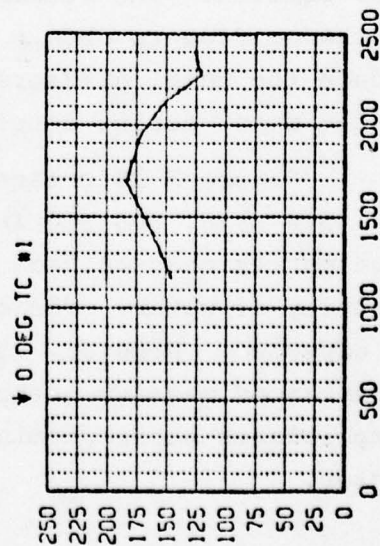
MODEL TI-7 WATER

Time = 42.97 to 48.00 Sec



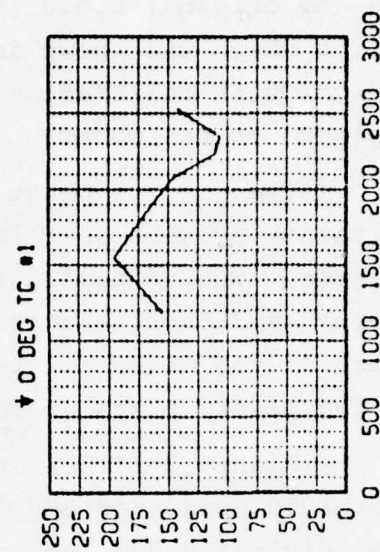
MODEL TI-1 DUST

Time = 27.23 to 30.30 Sec



MODEL TI-6 DUST AND WATER

Time = 36.07 to 38.20 Sec



MODEL SURFACE TEMPERATURE (°R)

FIGURE 3-16. STAGNATION POINT (0 DEGREES, TC #1) HEAT TRANSFER FOR RUN 2

gas sampler in operation, so no direct evidence exists to prove that water actually impinged on the model. This run was the original 0.020 inch straight-through water orifice design which was shown in Section 3.3.2 to atomize water on injection in calibration tests; and thus, no water may have impinged on the model!

The conclusion at this point was that a large uncertainty existed as to the presence of water at the test section. The recommendation was to reduce the total enthalpy (and thus, the tendency for water vaporization) and increase the mass flow of  $H_2O$  to attempt to retain the water in the liquid state at the test section.

Figure 3-17 presents the results for the Run 3 nominal 1000 psia, 500 Btu/lb conditions. This run again used the original 0.020 inch straight-through orifice design but more water was injected than on Run 2. In this case, there is some evidence of a slight cooling effect of the water. The dust only model shows a chemistry effect above 2000°F as expected. No chemistry effect due to the water is evident up to 2000°F in this run. The conclusion at this point was again a lack of firm evidence that water was present in the test section. The recommendation was to increase the size of the orifice to obtain higher water mass flow rates and to reduce the total pressure to maximize the potential survival of the water during acceleration by the air flow.

Figure 3-18 presents the results for the Run 4 nominal 500 psia, 500 Btu/lb conditions. The 0.0625 inch straight-through orifice design was used to inject a larger quantity of water. The clear air and dust only response was as expected. However, the water only and dust/water models experienced massive quenching. These models did not reach temperatures where chemistry would be expected to be a factor.

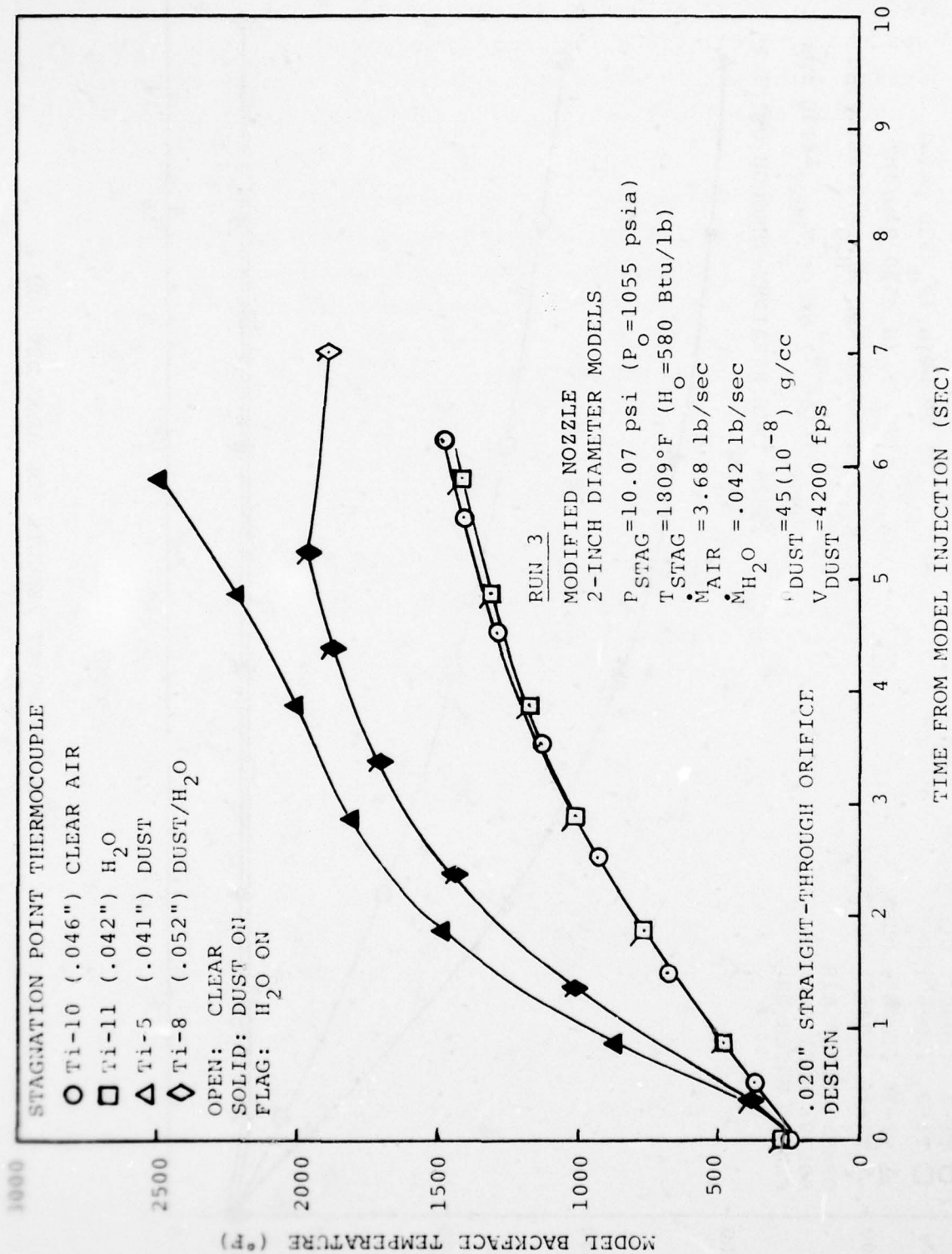


FIGURE 3-17. STAGNATION POINT RESULTS FOR AEDC DET RUN 3



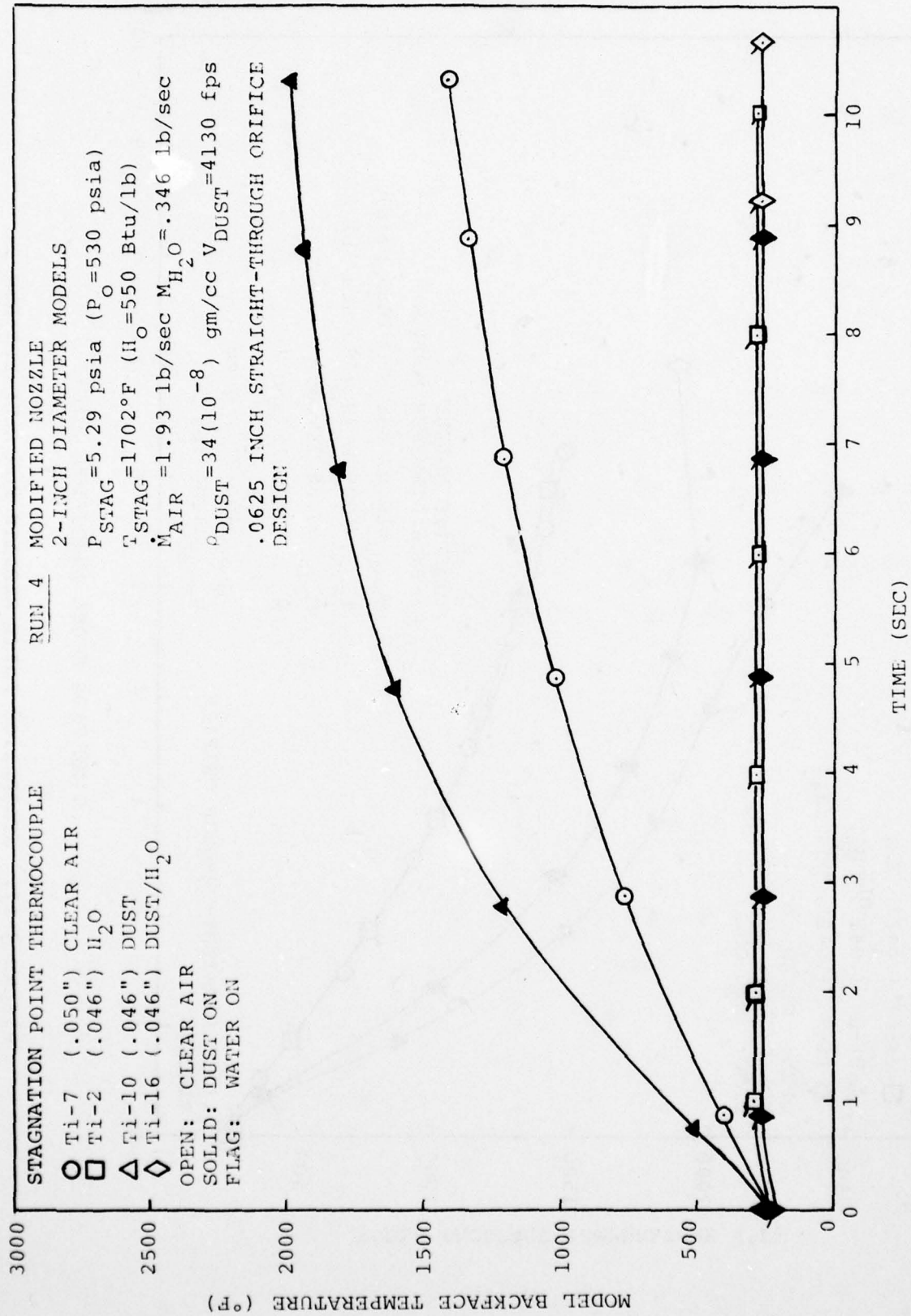


FIGURE 3-18. STAGNATION POINT RESULTS FOR AEDC DET RUN 4

The recommendation at this point was to perform the extensive bench calibration tests of the water orifice as described in Section 3.3.2 to arrive at a better orifice design prior to repeating the previous test conditions. In addition, the gas sampler was designed and implemented to quantify the water content of the gas.

Figures 3-19 and 3-20 present the results for the Run 5 nominal 500 psia, 500 Btu/lb conditions. This run used the 0.020 inch counterbored orifice design to attain a lower water injection rate and to reduce the dispersion of the water jet as it emerged from the orifice. This run used the gas sampler model. The primary purpose for collecting gas samples was to measure the total water content in the sample to allow a comparison of the water/air mass ratio of the sample to the water/air ratio determined by flow rate measurements. Two samples were collected during each run: one sample was analyzed for total water content and the other for species components. Water content was determined by Karl-Fisher titration and component analysis by use of a gas chromatograph. The results of the water content and component analyses are given in Table 3-4. For Run 5, the water/air mass ratio of injected water was  $1.54 \times 10^{-2}$ , and the water/air ratio of the sample was  $6.54 \times 10^{-3}$  or 42.5 percent of the injected value. The test procedure was also changed for Run 5 compared to preceding runs. Here, the models with water were preheated with clear air or dust to high temperature prior to water injection.

Figure 3-20 shows the heat transfer rate at  $1500^{\circ}\text{R}$  to be reduced from  $20 \text{ Btu/ft}^2 \text{ sec}$  for clear air to  $5 \text{ Btu/ft}^2 \text{ sec}$  for the water only model (water was introduced at  $\sim 1300^{\circ}\text{R}$ ). Note that dust was inadvertently turned on and accounts for the high temperature "turn-around" in heat transfer rate for

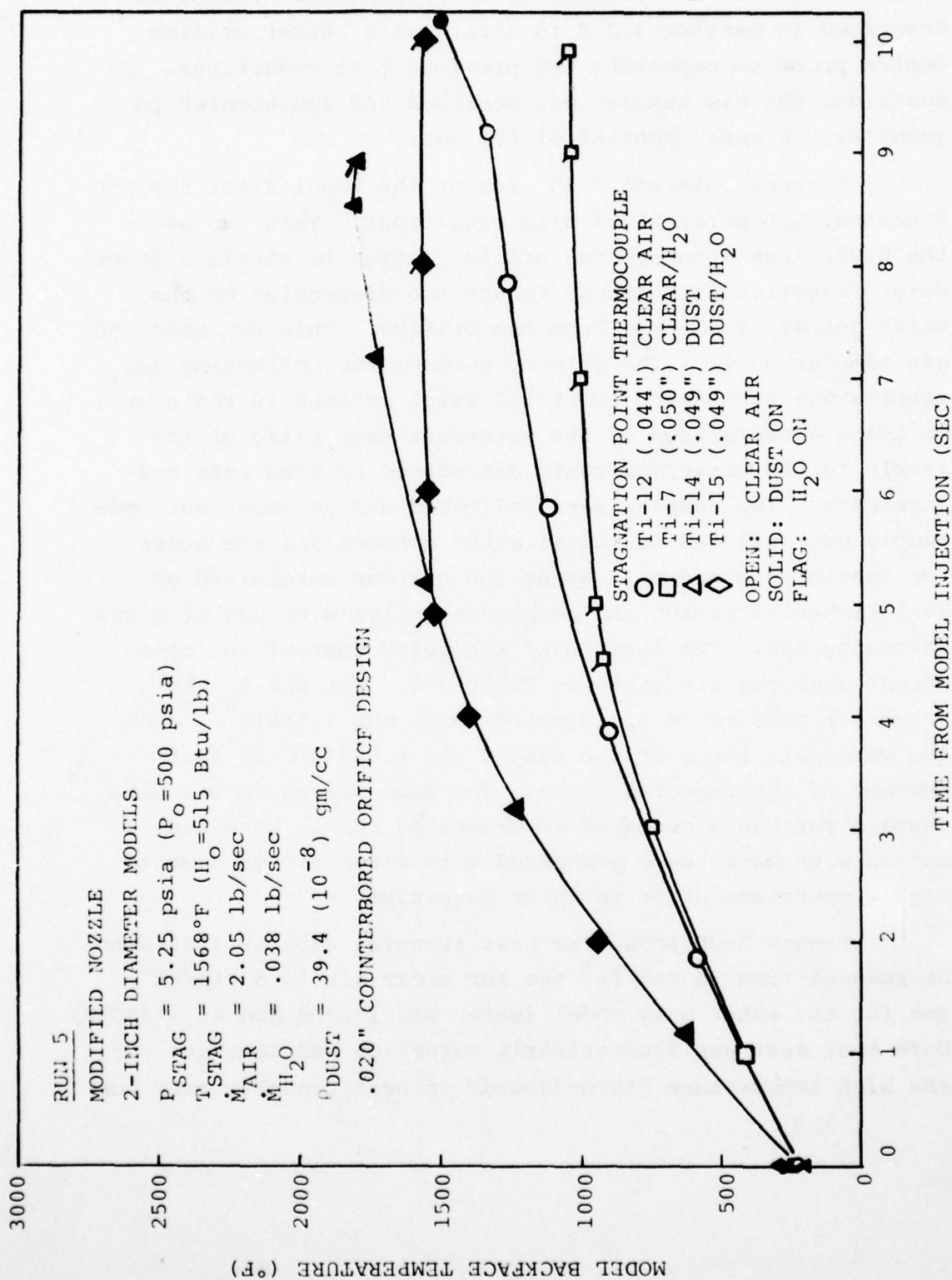


FIGURE 3-19. STAGNATION POINT RESULTS FOR AEDC DET RUN 5



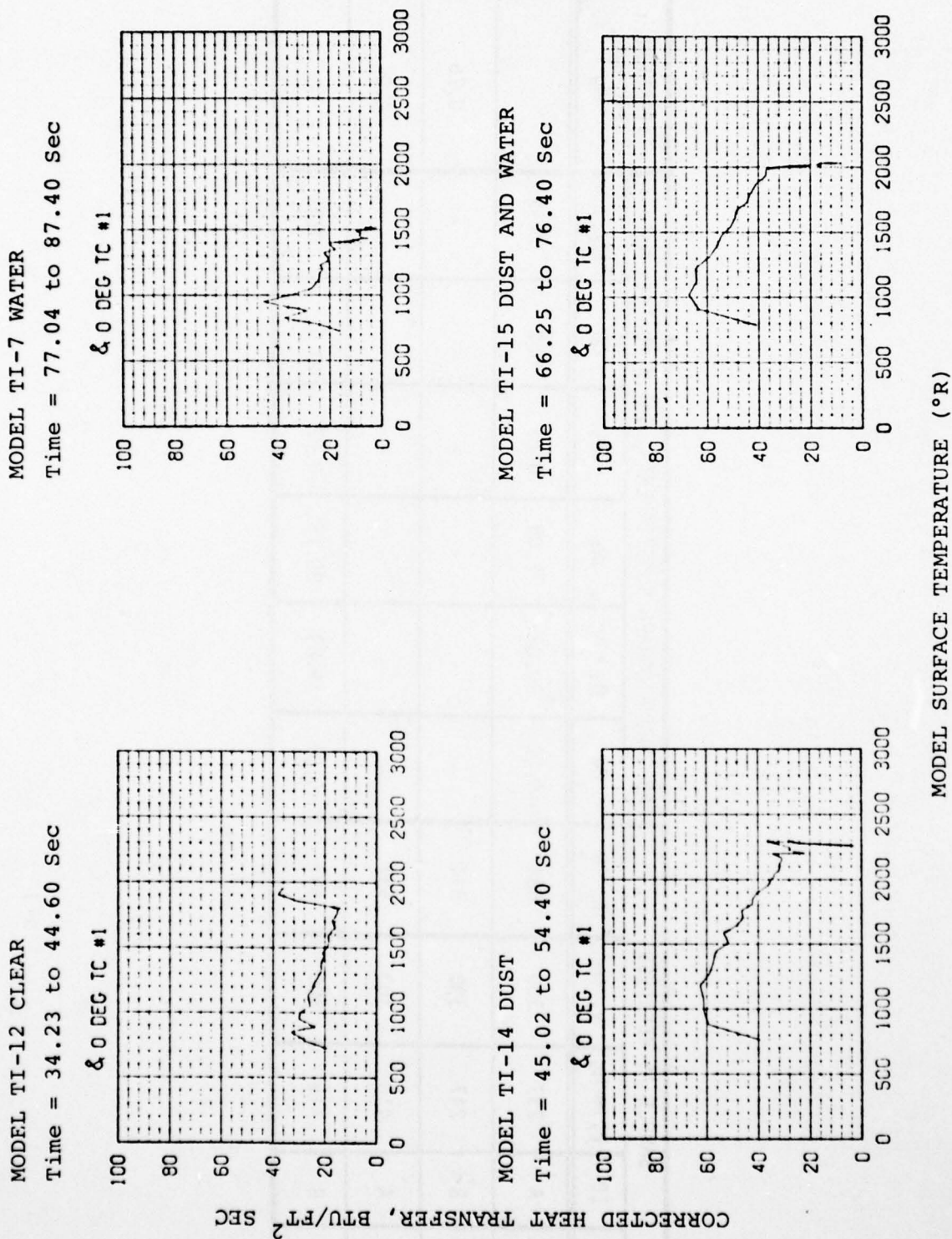


FIGURE 3-20. STAGNATION POINT HEAT TRANSFER FOR RUN 5

TABLE 3-4.  
RESULTS OF GAS SAMPLE ANALYSIS

SAMPLE AS RECEIVED				GAS CHROMATOGRAPH CONSTITUENTS, Vol.% (Unless Noted)						TITRATION, TOTAL H <sub>2</sub> O, mg
RUN	ID	P, mm Hg	v, cm <sup>3</sup>	T, °R	He	O <sub>2</sub> + Ar	N <sub>2</sub>	CO <sub>2</sub>	CO	NO <sub>x</sub> , ppm
5	A	237	300	534	0.02	20.08	78.08	0.07	0.01	2652
5	B	247	300	534	-	-	-	-	-	-
6	A	416	300	537	-	-	-	-	-	0.76
6	B	415	300	537	<0.01	19.89	80.15	0.07	<0.01	10323
										4.0
										-

the clear air model. Examination of the dust and the dust and water model responses also shows a cooling effect. Water was introduced at the end of the dust only model run and accounts for the significant heat transfer reduction at  $\sim 2200^{\circ}\text{R}$ . Water was introduced at  $\sim 2000^{\circ}\text{R}$  on the dust and water model and accounts for the significant heat transfer reduction observed. No chemistry effect of water is observed for these models which experienced bulk temperatures to  $\sim 2000^{\circ}\text{R}$ .

The preliminary conclusion at this point was that, since water was confirmed at the test section, there is no net effect of water on titanium surface chemistry, at least up to  $\sim 2000^{\circ}\text{R}$  temperatures. The recommendation was to simulate higher total enthalpies to confirm or deny this preliminary conclusion.

Figures 3-21 and 3-22 present the results for the Run 6 nominal 1000 psia, 800 Btu/lb conditions. The 0.020 inch counterbored orifice design was used. This run was a repeat of Run 2 except the dust concentration is lower and the water injection rate is higher. This run also had the gas sampler which showed that water was impinging on the model. For Run 6, the water/air ratio injected was  $1.99 \times 10^{-2}$ , and the water/air ratio for the sample was  $2.06 \times 10^{-2}$  or 103.4 percent of the injected value. These results for the 5 degree off-stagnation thermocouple location show the expected surface chemistry effect for the dust only model above  $\sim 2200^{\circ}\text{R}$ . The effect of adding water is shown to be a net cooling effect for both the water only and dust/water model. The preliminary conclusion was that water does not augment the surface chemistry for this intermediate total enthalpy flow condition. The recommendation was to conduct a high enthalpy flow run to further confirm or deny this preliminary conclusion.



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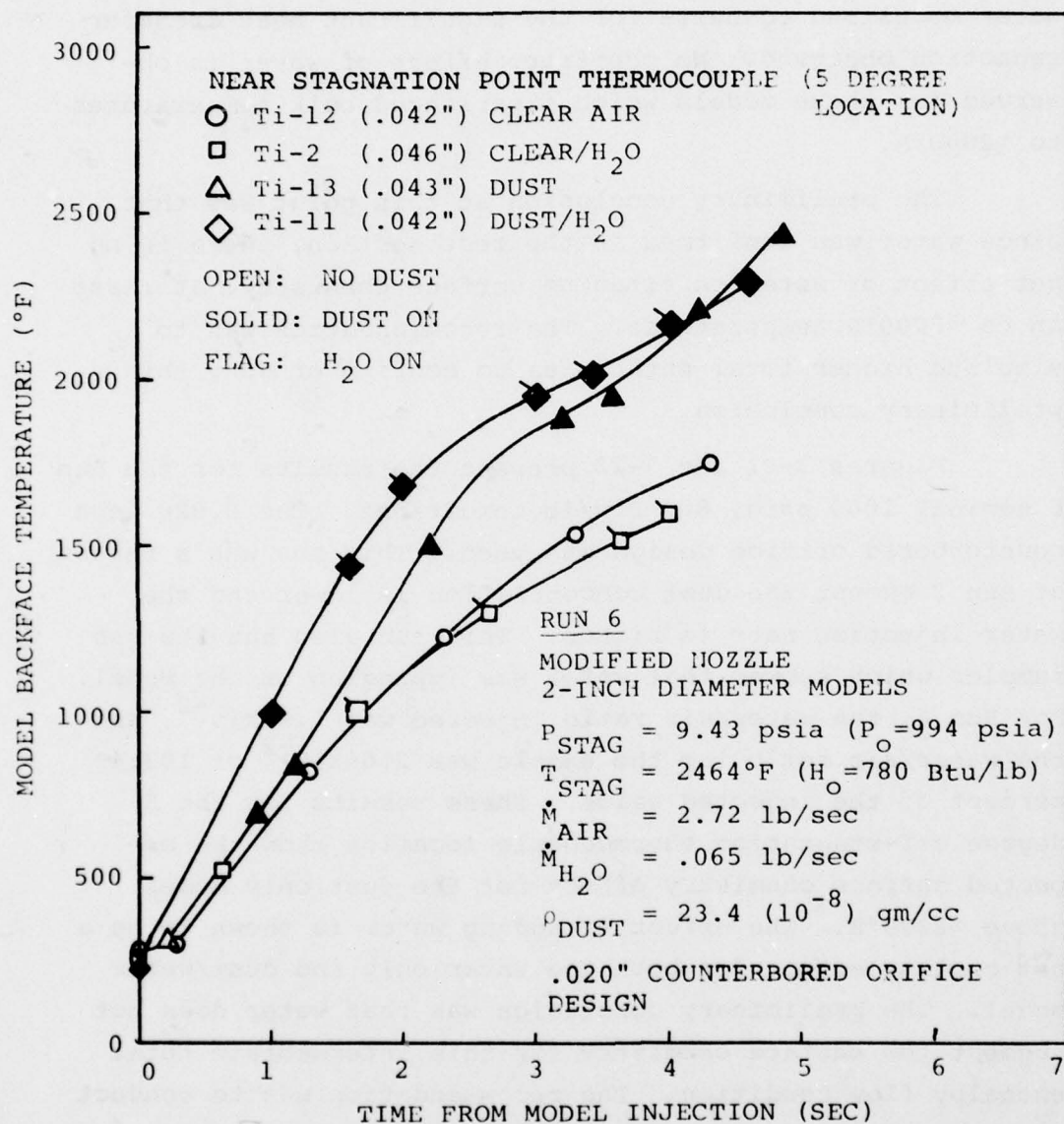
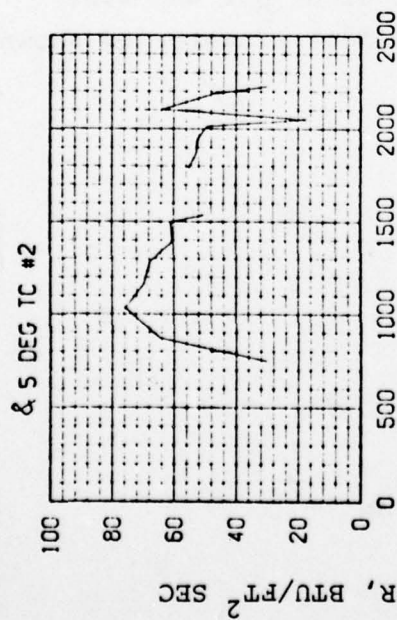
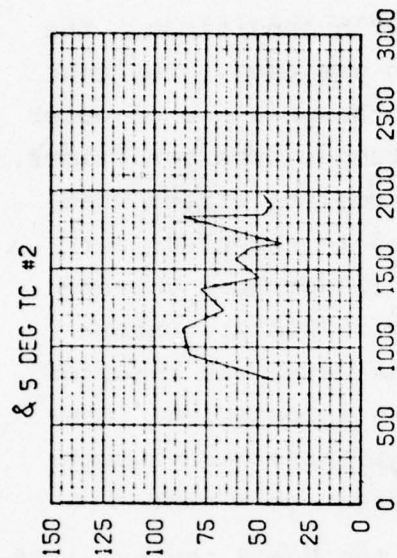


FIGURE 3-21. STAGNATION POINT RESULTS FOR AEDC DET RUN 6

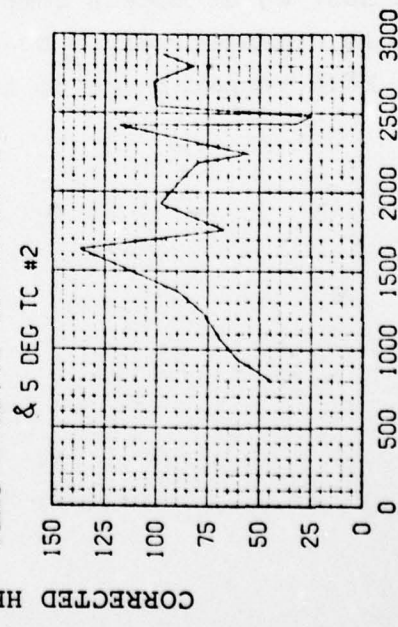
MODEL TI-12 CLEAR  
Time = 29.86 to 34.30 Sec



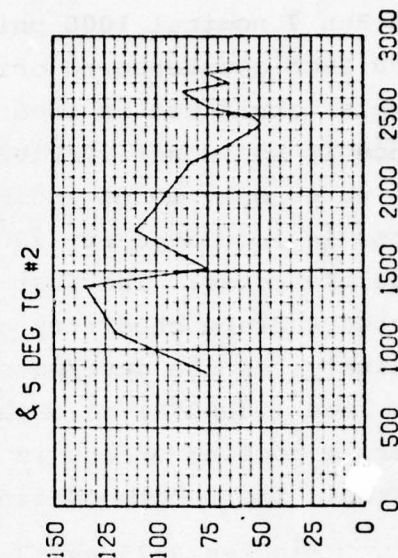
MODEL TI-2 WATER  
Time = 49.55 to 53.40 Sec



MODEL TI-13 DUST  
Time = 39.02 to 43.80 Sec



MODEL TI-11 DUST AND WATER  
Time = 44.23 to 49.00 Sec



MODEL SURFACE TEMPERATURE (°R)

FIGURE 3-22. STAGNATION POINT (5° LOCATION) HEAT TRANSFER FOR RUN 6

Figures 3-23 and 3-24 present the stagnation point backface temperature and surface heat transfer results for the Run 7 nominal 1000 psia, 1800 Btu/lb conditions. The .020 inch counterbored orifice design was used. The gas sampler could not be used to confirm the presence of water since it would not survive the high temperature conditions. The water only model indicates a net cooling effect when water is initiated at  $\sim 2500^{\circ}\text{R}$  compared to the clear air model response. The dust only model illustrates the expected surface chemistry effects above  $\sim 2200^{\circ}\text{R}$ . Unfortunately, on the dust/water model, the water was injected too late ( $\sim 3000^{\circ}\text{R}$ ) to obtain extensive information. However, a cooling effect is suggested at these high temperatures. The recommendation was to repeat this run.

Figures 3-25 and 3-26 present the Run 8 nominal 1000 psia, 1800 Btu/lb results for the repeat of Run 7. Test conditions were essentially identical to Run 7 except that 2.0 inch models were used. Again, the gas sampler could not be used. The results show the same increased surface chemistry from dust above  $\sim 2200^{\circ}\text{R}$ . A decreased heat transfer effect of water is shown in Figure 3-26 for both the water and dust/water models compared to the clear air and dust models, respectively. No increased effect of water is shown for bulk temperatures up to  $\sim 3000^{\circ}\text{R}$ .



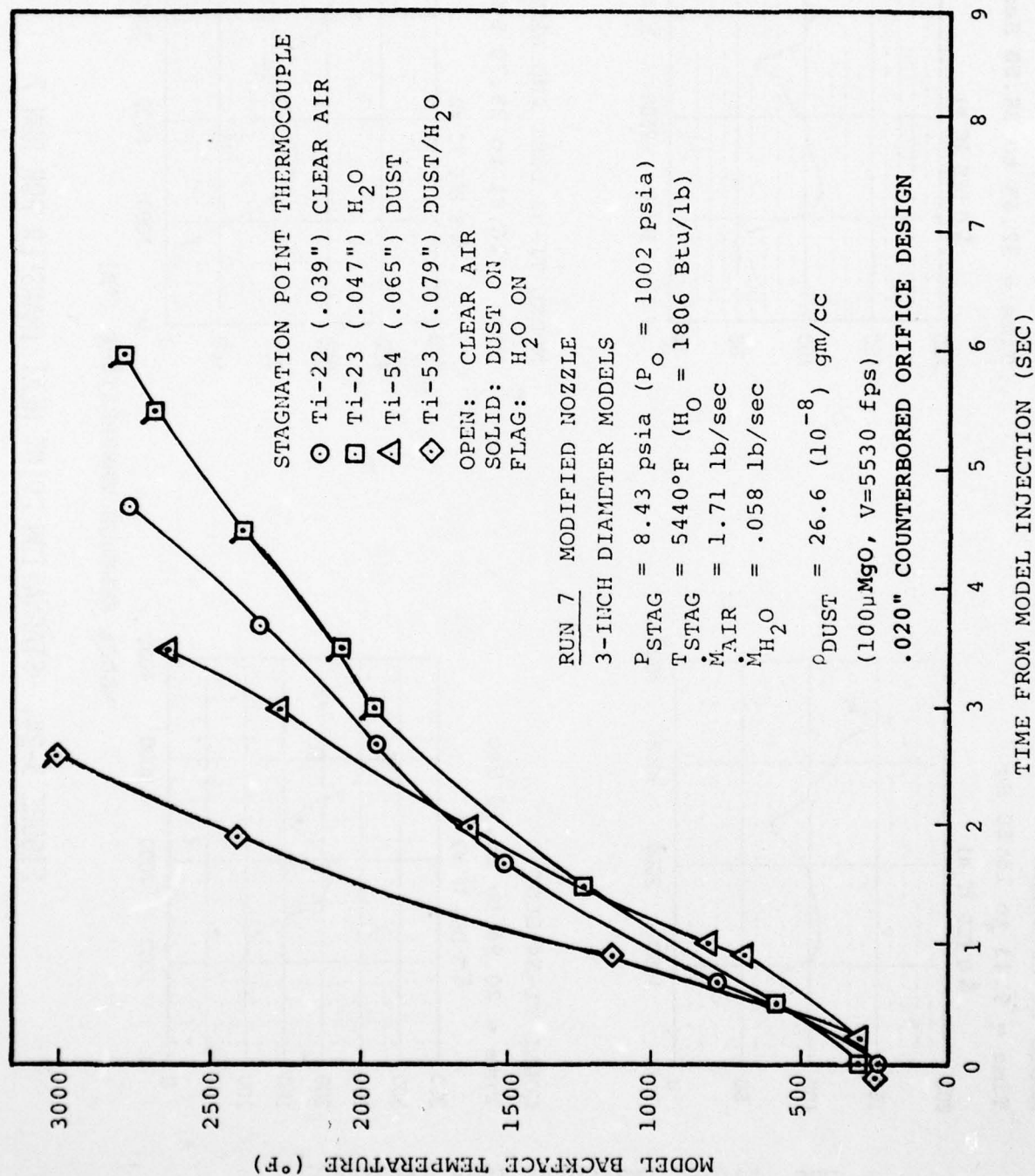
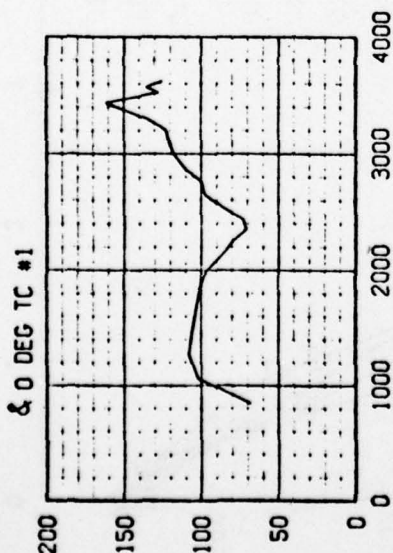


FIGURE 3-23. STAGNATION POINT RESULTS FOR AEDC DET RUN 7

CORRECTED HEAT TRANSFER, BTU/FT<sup>2</sup> SEC

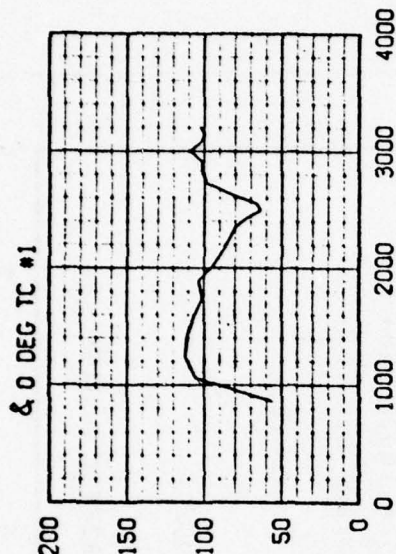
MODEL TI-22 CLEAR

Time = 9.43 to 15.60 Sec



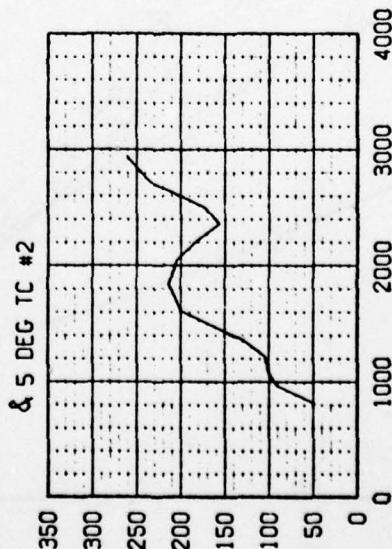
MODEL TI-23 WATER

Time = 32.65 to 38.50 Sec



MODEL TI-54 DUST

Time = 20.96 to 23.50 Sec



MODEL TI-53 DUST AND WATER

Time = 26.01 to 29.70 Sec

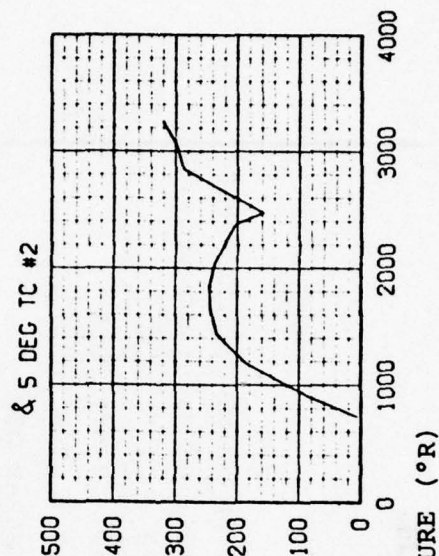


FIGURE 3-24. STAGNATION POINT HEAT TRANSFER FOR RUN 7

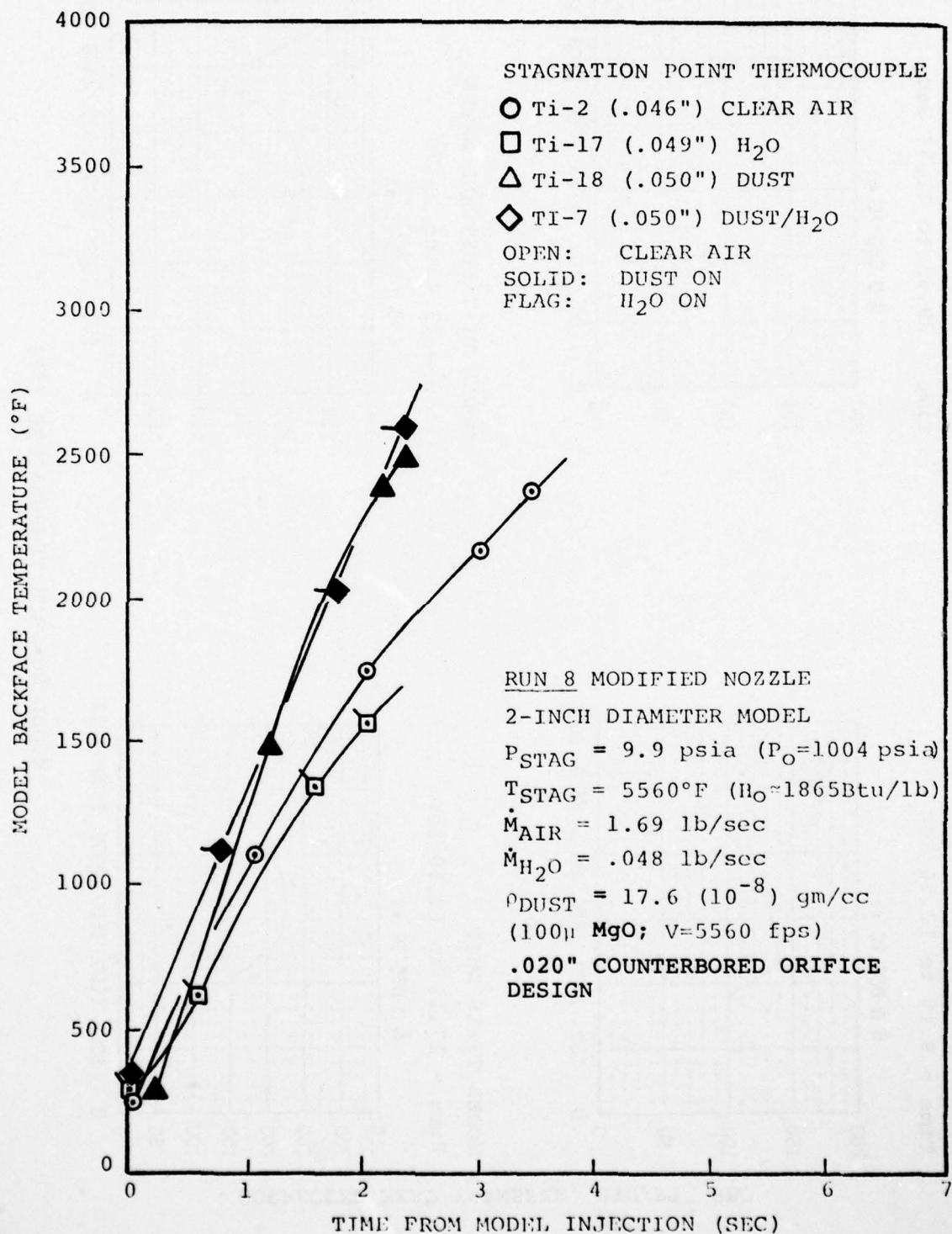
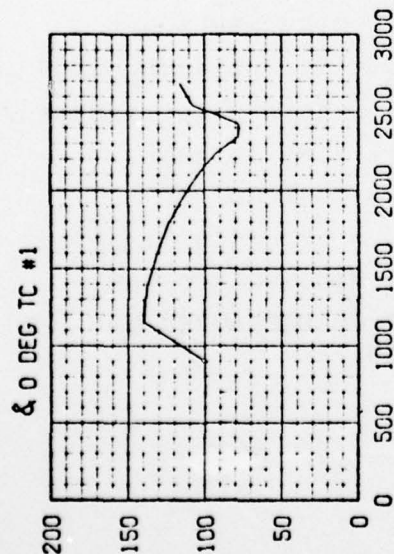


FIGURE 3-25. STAGNATION POINT RESULTS FOR AEDC DET RUN 8



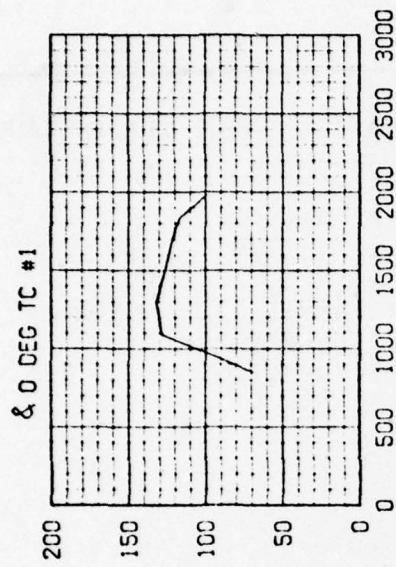
MODEL TI-2 CLEAR

Time = 9.16 to 12.50 Sec



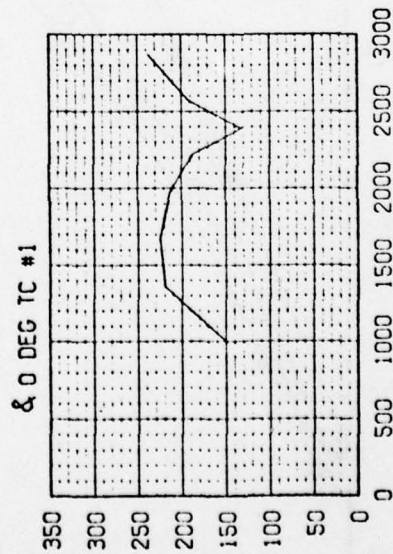
MODEL TI-17 WATER

Time = 29.65 to 31.50 Sec



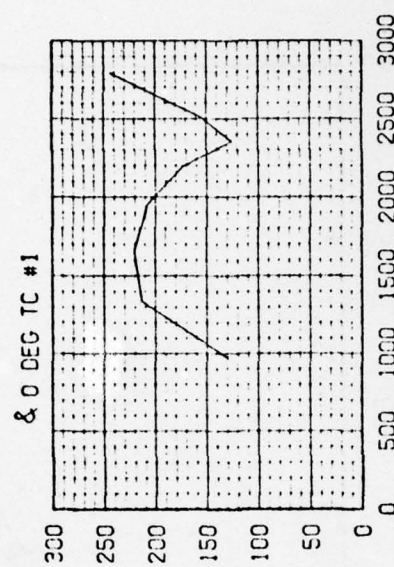
MODEL TI-18 DUST

Time = 17.11 to 19.20 Sec



MODEL TI-7 DUST AND WATER

Time = 23.43 to 25.70



MODEL SURFACE TEMPERATURE (°R)

FIGURE 3-26. STAGNATION POINT HEAT TRANSFER FOR RUN 8

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SCIENCE APPLICATIONS INC EL SEGUNDO CALIF  
TITANIUM RESPONSE TO SIMULATED NUCLEAR CLOUD PARTICLE ENVIRONME--ETC(U)  
AUG 77 L E DUNBAR, R M CLEVER, G H BURGHART DNA001-76-C-0366

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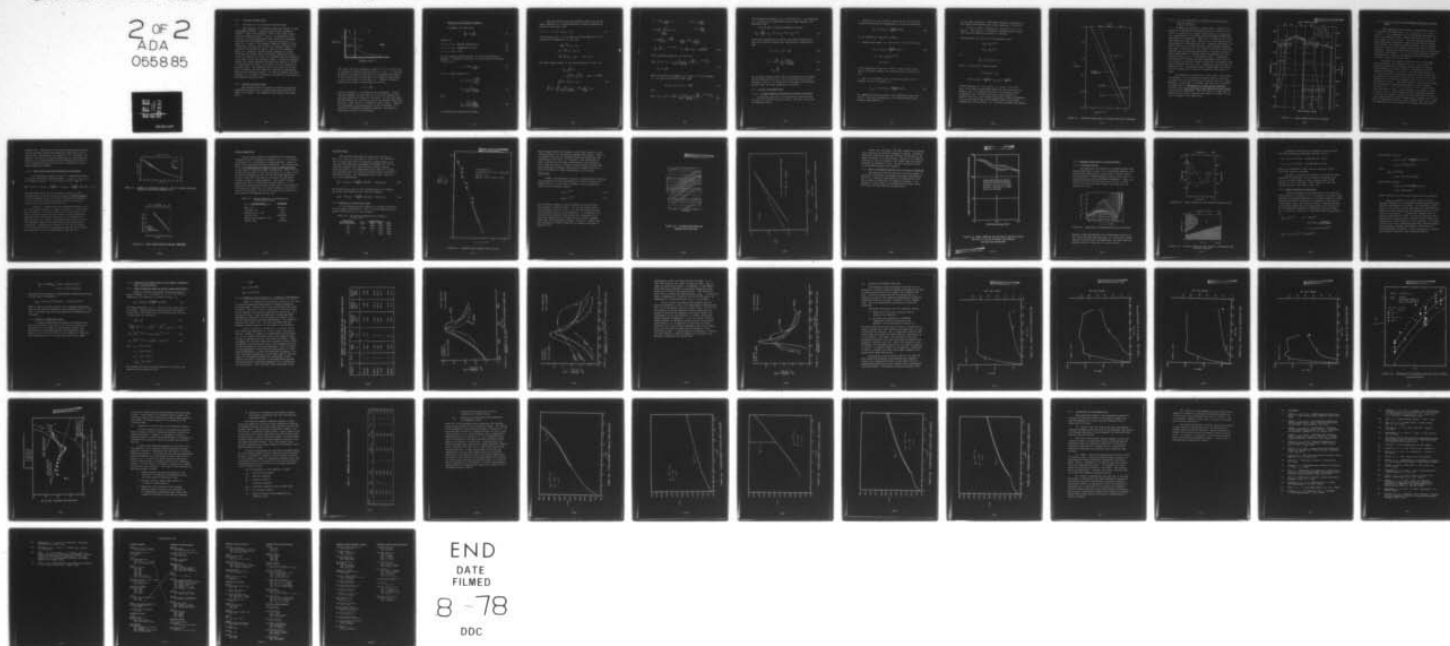
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#### 4.0 TITANIUM RESPONSE MODEL

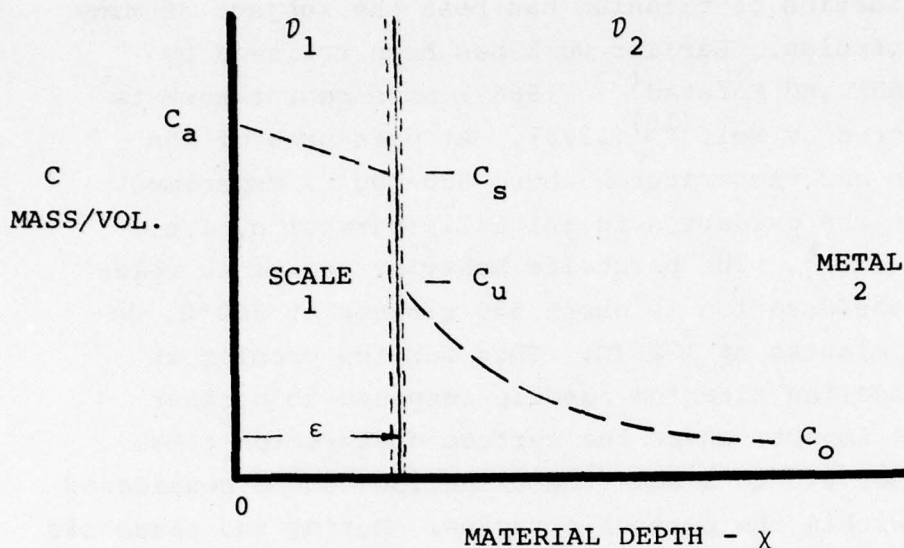
##### 4.1 Formulation of the Titanium Oxidation Model

The oxidation of titanium has been the subject of many experimental studies. Earlier work has been reviewed by Hauffe<sup>(8)</sup> (1965) and Kofstad<sup>(9)</sup> (1966); more recent work is briefly discussed by Wolf<sup>(10)</sup> (1975). At pressures of the order of 1 atm and temperatures above 600-700°C, experiment has shown that the oxidation is initially parabolic, i.e., mass gain  $\sim (\text{time})^{\frac{1}{2}}$ . The parabolic behavior regime is relatively long; the duration is about 500 minutes at 800°C, decreasing to 8 minutes at 1200°C. Thus for the problem at hand, i.e., modeling titanium nosetip response to nuclear cloud particle impact, where the surface obscuration times are of the order 0.1 to 1 sec, the oxidation can be considered to be wholly within the parabolic regime. During the parabolic regime, two oxygen consuming processes are observed to occur: (a) dissolution of oxygen in the metal, and (b) formation of an oxide scale. Our objective here is to review the literature to assemble the data required to develop an engineering model of the oxidation process. In order to identify the data required, it is helpful to present an introductory discussion of the proposed oxidation model.

##### 4.1.1 Proposed Oxidation Model

The proposed model for parabolic oxidation postulates simultaneous formation of a compact scale and dissolution of oxygen in the metal. The schematic below depicts the situation.





This model was first proposed by Wagner<sup>(11)</sup>, and has been used to interpret zirconium oxidation data in (12,13). In these applications the model has been used in a semi-empirical fashion to avoid requiring the knowledge of the oxygen concentration at the outer surface of the scale,  $C_a$ . Instead a parabolic growth law for scale is postulated in the form

$$\epsilon = 2 \gamma \sqrt{D_1 t}$$

where the constant  $\gamma$  is determined from experiment. Following this approach the next step is to solve the species conservation equation in region 2, the metal. In our final model for engineering use, this solution will be obtained numerically since  $D_2 = D_2(T)$  and  $T$  is a function of both  $x$  and  $t$ . However, for the purpose of evaluating data in the literature, it is sufficient to consider isothermal oxidation, for which an analytical solution can be obtained.

### Solution for Isothermal Oxidation

In Region 2 we must solve

$$\frac{\partial c}{\partial t} = D_2 \frac{\partial^2 c}{\partial x^2} \quad (2)$$

subject to

$$t = 0, c = c_0, \text{ assumed constant here} \quad (3)$$

$$x = \epsilon, c = c_u, \text{ independent of time} \quad (4)$$

$$x \rightarrow \infty, c = c_0 = 0 \text{ say} \quad (5)$$

For this moving boundary problem, we follow the method of Neumann. A solution to Equation (2) which satisfies Equations (3) and (5) is

$$c = A \operatorname{erfc} \frac{x}{2\sqrt{D_2 t}} \quad (6)$$

at  $x = \epsilon$ , using Equation (4),

$$c_u = A \operatorname{erfc} \frac{2\gamma\sqrt{D_1 t}}{2\sqrt{D_2 t}}$$

$$A = \frac{c_u}{\operatorname{erfc} \gamma \sqrt{D_1/D_2}} \quad (7)$$

Thus

$$\frac{c}{c_u} = \frac{\operatorname{erfc} \frac{x}{2\sqrt{D_2 t}}}{\operatorname{erfc} \gamma \sqrt{D_1/D_2}} \quad (8)$$

is the desired concentration profile.

Next we postulate that the parabolic growth law for the scale, Equation (1) is associated with a linear concentration profile in the scale, then

$$0 < x < \epsilon, \quad c = c_a - \frac{x}{\epsilon} (c_a - c_s) \quad (9)$$

In the limit of  $D_2 \rightarrow 0$  it is easy to see that Equation (5) is consistent with Equation (1), for then

$$\begin{aligned} \rho \frac{d\epsilon}{dt} &= \frac{D_1}{\epsilon} (c_a - c_s) \\ \epsilon d\epsilon &= \frac{D_1}{\rho} (c_a - c_s) dt \\ \frac{\epsilon^2}{2} &= \frac{D_1}{\rho} (c_a - c_s) t \quad \text{or } \epsilon \propto \sqrt{t} \end{aligned}$$

The total oxygen present in the scale and metal at time  $t$  is

$$\begin{aligned} M_{O_2} &= \int_0^{\infty} c \, dx \\ &= \int_0^{\epsilon} c \, dx + \int_{\epsilon}^{\infty} c \, dx \quad \text{with } \epsilon = 2\gamma\sqrt{D_1 t} \\ \int_0^{\epsilon} c \, dx &= \frac{1}{2} (c_a + c_s) \epsilon \\ \int_{\epsilon}^{\infty} c \, dx &= \int_{\epsilon}^{\infty} \left\{ \frac{c_u}{\operatorname{erfc} \gamma \sqrt{D_1/D_2}} \operatorname{erfc} \frac{x}{2\sqrt{D_2 t}} \right\} dx \end{aligned} \quad (10)$$



$$= A \operatorname{erfc} \frac{x}{2\sqrt{D_2 t}} dx$$

$$\text{Let } \eta = \frac{x}{2\sqrt{D_2 t}}$$

$$= A 2\sqrt{D_2 t} \int_{\frac{\epsilon}{2\sqrt{D_2 t}}}^{\infty} \operatorname{erfc} \eta d\eta$$

$$d\eta = \frac{dx}{2\sqrt{D_2 t}}$$

$$= A 2\sqrt{D_2 t} \left[ \frac{1}{\sqrt{\pi}} e^{-\frac{\epsilon^2}{4D_2 t}} - \frac{\epsilon}{2\sqrt{D_2 t}} \operatorname{erfc} \frac{\epsilon}{2\sqrt{D_2 t}} \right]$$

$$= A \left[ 2 \frac{D_2 t}{\pi} e^{-\gamma^2 D_1/D_2} - 2 \gamma \sqrt{D_1 t} \operatorname{erfc} \gamma \sqrt{D_1/D_2} \right] \quad (11)$$

Thus, combining Equations (10) and (11),

$$M_{O_2} = \frac{1}{2} (c_a + c_s) + \frac{c_u}{\operatorname{erfc} \gamma \sqrt{D_1/D_2}} 2 \sqrt{\frac{D_2 t}{\pi}} e^{-\gamma^2 D_1/D_2} - c_u 2 \gamma \sqrt{D_1 t} \quad (12)$$

Next we eliminate the unknown  $c_a$  in favor of  $\gamma$ ; if we assume  $c_a \approx c_s$  this is particularly easy, then

$$\frac{1}{2} (c_a + c_s) \epsilon = c_s 2 \gamma \sqrt{D_1 t} \quad (13)$$

and

$$M_{O_2} = (c_s - c_u) 2 \gamma \sqrt{D_1 t} + \frac{c_u}{\operatorname{erfc} \gamma \sqrt{D_1/D_2}} 2 \sqrt{\frac{D_2 t}{\pi}} e^{-\gamma^2 D_1/D_2} \quad (14)$$

which agrees with Equation (21) in Reference (9). The assumption  $c_a \approx c_s$  proves to be sufficiently good to make Equation (12) generally valid.

For the rate of oxygen consumption we write

$$\dot{M}_{O_2} = \frac{dM_{O_2}}{dt} = K_o t^{-1/2} = K_f t^{-1/2} + K_s t^{-1/2} \quad (15)$$

where rate constants  $K_o$ ,  $K_f$  and  $K_s$  have been introduced for the total oxidation, oxide film, and solution, respectively. Thus

$$K_f = (c_s - c_u) \gamma \sqrt{D_1} \quad (16)$$

$$K_s = c_u \sqrt{\frac{D_2}{\pi}} \frac{e^{-\gamma^2 D_1/D_2}}{\operatorname{erfc} \gamma \sqrt{D_1/D_2}} \quad (17)$$

$$\approx c_u \sqrt{\frac{D_2}{\pi}} \quad (18)$$

The preceding analysis shows that the parameters of the model are the concentrations  $c_a$ ,  $c_s$  and  $c_u$  and the diffusion coefficients  $D_1$  and  $D_2$ . In order to use the model for engineering analysis data for these parameters is required.

#### 4.1.2 Survey of Available Data

##### 4.1.2.1 $D_2$ The Diffusion Coefficient of Oxygen in Titanium

Considerable data for  $D_2$  for unalloyed titanium exists, but data for titanium alloys is sparse. The most useful data is summarized below.

1. Kofstad et al (14) derived a value for  $D_2$  for unalloyed titanium neglecting the consequences of oxide film formation,

$$D_2 = 0.5 \exp \left( - \frac{51,000}{RT} \right) \text{ cm}^2/\text{s} \quad (19)$$

in the temperature range 800 - 1200°C.

2. Shamblen and Redden (15) obtained for Ti-6Al-2Sn-4Zr-2M<sub>O</sub>

$$D_2 = D_O \exp \left( - \frac{48,000}{RT} \right) \text{ cm}^2/\text{s} \quad (20)$$

$$D_O = 147 [\text{O}_2 \text{ ppm}]^{-0.742}$$

$$\approx 062 \text{ cm}^2/\text{s}$$

in the temperature range 300 - 870°C. These authors found that  $\text{O}_2$  increases somewhat with substitutional alloying content.

3. Rosa (9) determined  $D_2$  for  $\alpha$ -titanium from the rate of movement of the  $\alpha$ - $\beta$  interface as

$$D_{2(\alpha)} = 0.778 \exp \left( - \frac{48,600}{RT} \right) \text{ cm}^2/\text{s} \quad (21)$$

for commercially pure titanium in the temperature range 932 - 1142°C. Rosa also determined  $D_2$  for  $\beta$ -titanium from micro-hardness measurements as



for the same conditions. Rosa makes favorable comparisons of his results with earlier data in the literature, (17,18,19).

Figure 4-1 shows a comparison of Equations (18, 19, 20 and 21). Also shown is a "corrected" Kofstad equation rederived from his oxidation rate data, as follows:

From Equations (13) and (17), for dissolution only.

$$\dot{M}_{O_2} = K_s t^{-1/2}$$

$$M_{O_2} = 2K_s t^{1/2}$$

or

$$M_{O_2}^2 = \frac{4}{\pi} c_u^2 D_2 t \equiv K_p t$$

For  $c_u = 0.641 \text{ gm/cm}^3$  (derived below)

$$0.523 K_p D_2 = K_p$$

$$0.523 D_O \exp \left( - \frac{51,000}{RT} \right) = A_p \exp \left( - \frac{51,000}{RT} \right)$$

Kofstad obtained  $A_p = 3.2$ , thus  $D_O = 3.2/5.23 = 6.12 \text{ cm}^2/\text{s}$  which is an order of magnitude higher than the value given by Equation (19). We conclude that there is a numerical error in Equation (19). We also note that we would expect the Kofstad value of  $D_2$  to be higher than those of Rosa and Shamblen since in the former case it was assumed that all the oxygen consumed went into solution, i.e., the  $\text{TiO}_2$  formation was ignored.

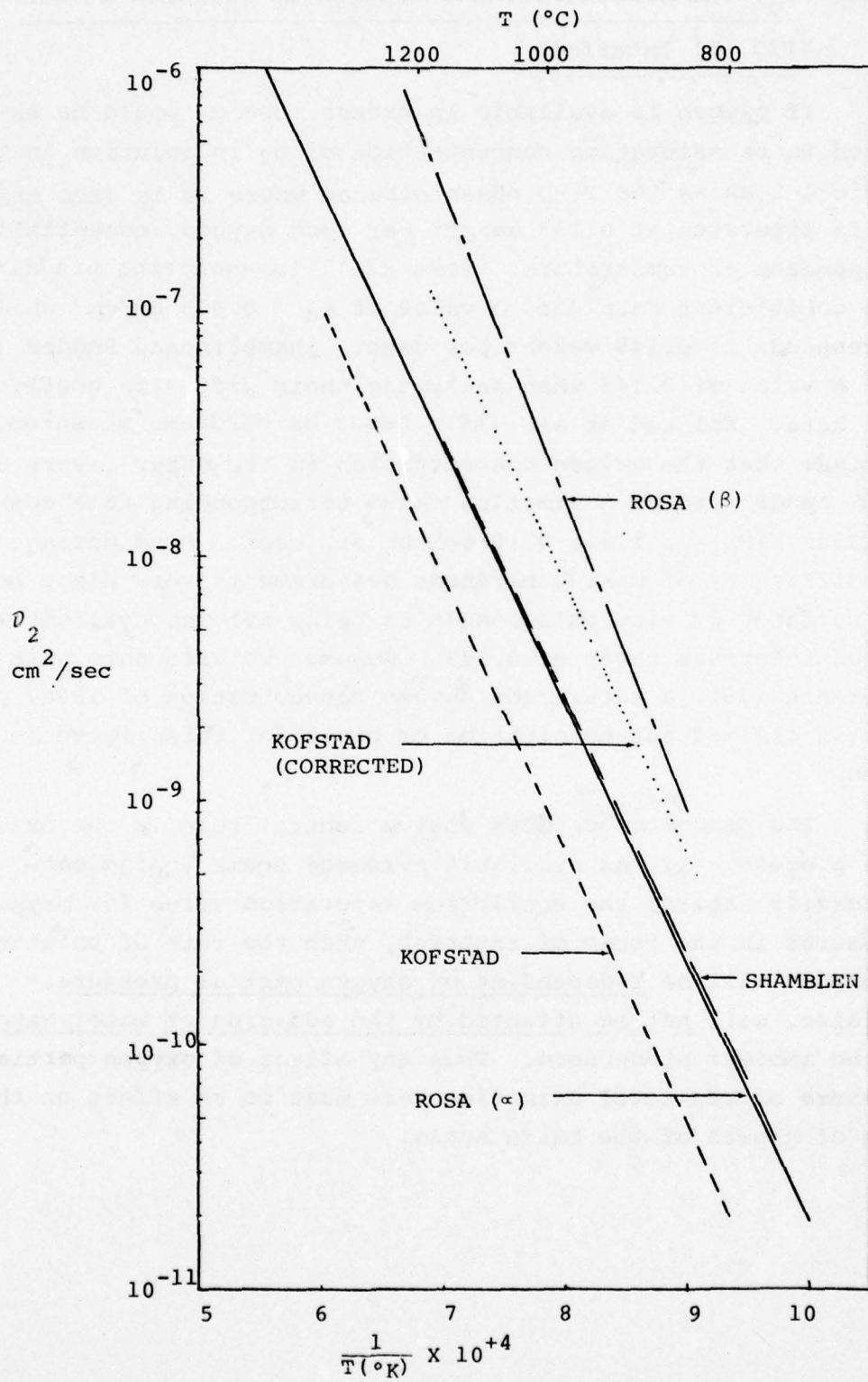


FIGURE 4-1. DIFFUSION COEFFICIENT IN TITANIUM FROM THE LITERATURE

#### 4.1.2.2 $c_u$ , The Concentration of Oxygen in Titanium at the $\text{TiO}_2$ -Ti Interface

If oxygen is available in excess then  $c_u$  would be expected to be saturation concentration of  $\text{O}_2$  in solution in Ti. Figure 4-2 shows the Ti-O phase diagram where it is seen that  $\alpha\text{Ti}$  is saturated at 0.143 weight per cent oxygen, essentially independent of temperature. Rosa (16), in analyzing his diffusion coefficient data used a value of  $c_u = 0.665 \text{ gm/cm}^3$  which corresponds to 0.148 weight per cent. Shamblin and Redden (15) used a value of 0.143 when analyzing their diffusion coefficient data. Kofstad et al. (14), based on hardness measurements, conclude that the oxygen concentration in the outer layers of metal tends towards a limiting value corresponding to a composition  $\text{TiO}_{0.35}$ , i.e., 0.10 weight per cent. Considering the difficulty of making hardness measurements very close to the surface, we view this result as being not inconsistent with a true interface value of 0.143. However we also note that in Reference (20), a saturation oxygen concentration of 10.02 per cent is claimed but no citation or basis for this figure is given.

The parameter  $c_u$  does play a central role in the oxidation process. If, as available evidence seems to indicate,  $c_u$  readily attains the equilibrium saturation value for oxygen pressures in the range of interest, then the rate of solution of oxygen will be independent of oxygen partial pressure, and also, will not be affected by the addition of water vapor to the ambient atmosphere. Thus any affect of oxygen partial pressure on the total oxidation rate must be an effect on the rate of growth of the oxide scale.



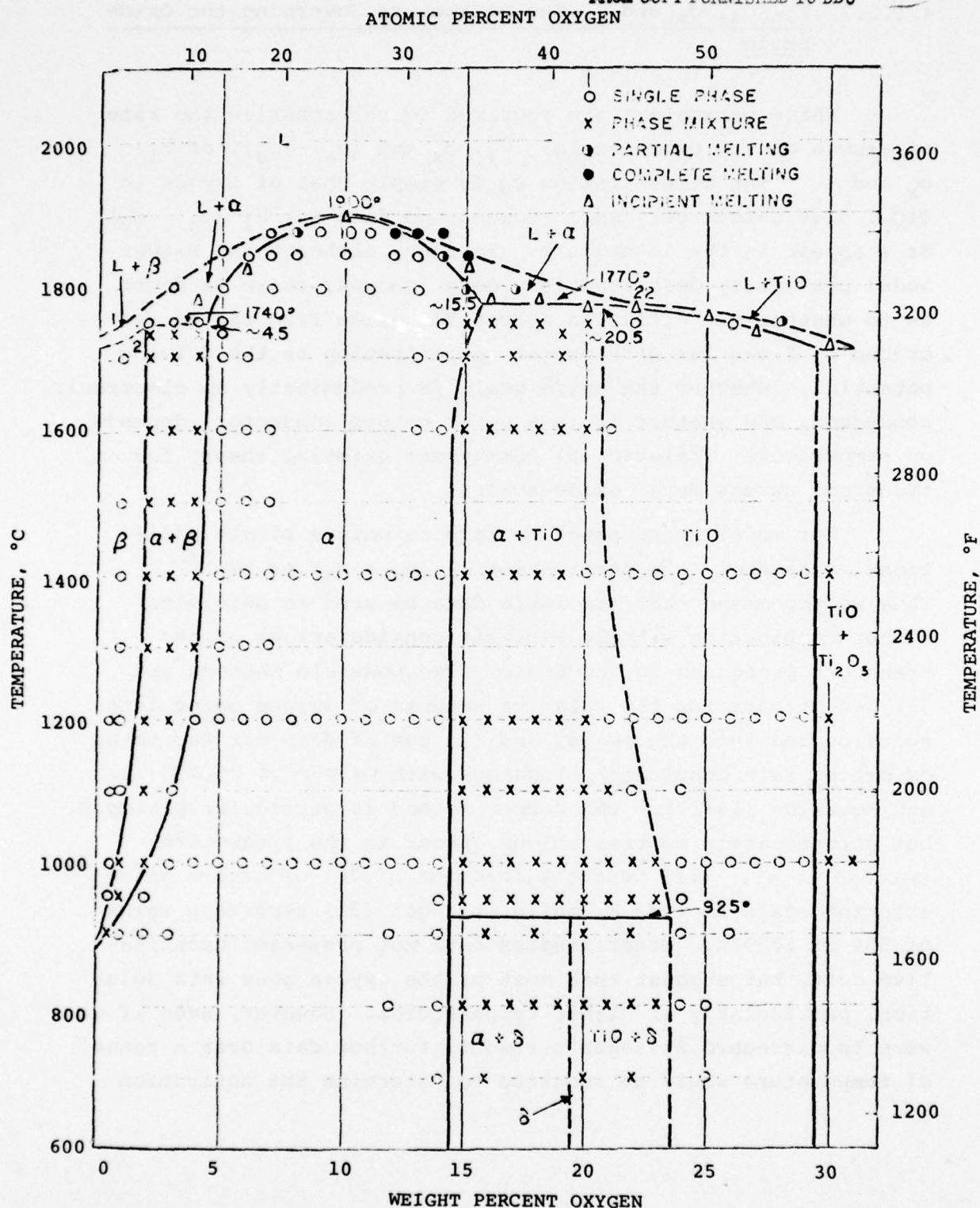


FIGURE 4-2. PHASE DIAGRAM FOR THE TI-O SYSTEM

#### 4.1.2.3 $D_1$ , $c_a$ , $c_s$ and $\gamma$ , The Parameters Governing the Oxide Scale

Three parameters are required to characterize the rate of growth of the oxide scale:  $D_1$ ,  $c_s$  and  $(c_a - c_s)$ , or  $D_1$ ,  $c_s$  and  $\gamma$ . The concentration  $c_s$  is simply that of oxygen in  $\text{TiO}_2$ , 0.40 weight per cent. However no data for  $D_1$  ( $c_a - c_s$ ) or  $\gamma$  appear in the literature. In fact, although the Wagner model previously described is widely ignored, there is doubt as to whether the diffusion across the oxide film can be described by Ficks law with oxygen concentration as the driving potential. Whether the oxide scale is predominately an electronic conductor, and whether it is a p- or n-type conductor, depends on temperature. Kofstad (9) summarizes existing theory for transport across metal oxide scales.

For modeling purposes we require only a single additional parameter, the combination  $D_1 (c_a - c_s)$  or  $\gamma D_1^{1/2}$ . Thus we recommend that available data be used to determine either combination without explicit considerations of the transport processes in the scale. Two possible methods are (1) use of data for the relative amounts of oxygen going into solution and into the scale, and (2) use of data for the total oxidation rate constant  $K_O$  together with values of  $D_2$  and  $c_u$ , and Equation (13-17). The former method is particularly simple but unfortunately contradictions appear in the literature. Kofstad et al. (14) report a fraction of 20% of oxygen going into the scale at 1173 K, while Stringer (21) reports a value of 55% at 1223 K. Other studies have not presented quantitative data, but suggest that most of the oxygen goes into solution, particularly at higher temperatures. However, even if we were to disregard Stringer's result, further data over a range of temperature would be required to determine the activation

energy of  $D_1$ . Application of the latter method requires selection of the most reliable and appropriate data for  $K_O$  and  $D_2$  since, again, contradictions do appear in the literature. For example, if we were to use the Kofstad data for  $K_O$  and Rosa's data for  $D_2$ , we would deduce that considerably more than 20% of the oxygen was going to form scale, in variance with the value reported by Kofstad.

#### 4.1.2.4 Data for $K_O$ , The Total Oxidation Rate Constant

For unalloyed titanium Stringer (21) compared the data of his own and several previous studies. Figure 4-3 taken from (21) shows his result. His correlation for  $K_P^2 (=4K_O^2)$  is

$$4K_O^2 = 1.007 \times 10^{-6} \exp \left( -\frac{25,400}{RT} \right) + 320 \exp \left( -\frac{61,800}{RT} \right) \text{ gm}^2/\text{cm}^4\text{s} \quad (23)$$

and concluded that  $D_1$  has an activation energy of 25,400 cal/mole while  $D_2$  has an activation energy of 61,800 cal/mole. It is of interest to note that  $K_f/K_O$  calculated from Equation (23) at 1223 K is close to unity and not 55% as quoted by Kofstad (9) as being obtained by Stringer.

Kofstad (9) compared the data obtained by Kofstad et al. (14) with previous studies, as shown in Figure 4-4: good agreement is apparent. The more recent data is that of Wolf (10). Figure 4-5 shows Wolf's data for "Type 1" unalloyed titanium with Stringer's correlation, Equation (22) and the data of Kofstad et al. (14). Within experimental error there is excellent agreement between Wolf's data points and the Stringer correlation. Comparison of Figures 4-3, 4-4 and 4-5 leads to the conclusion that the experimental data for  $K_O$  is reasonably consistent and well represented by Equation (23).



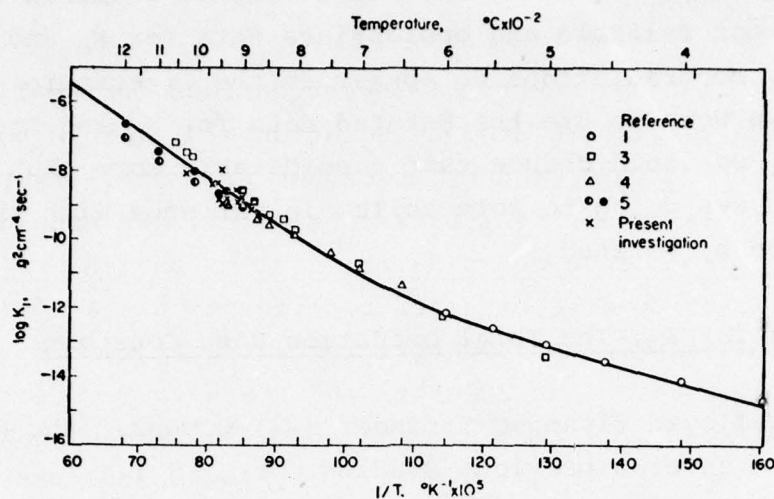


TABLE 4-3. SUMMARY OF SPECIMENS (Ti6AL-4V) USED TO COMPARE PREDICTED REACTION RATE WITH EXPERIMENT (10)

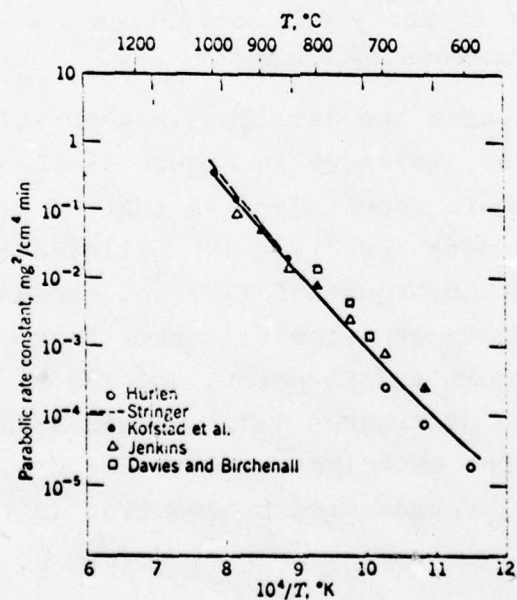


FIGURE 4-4. TOTAL OXIDATION RATE CONSTANT [KOFSTAD]

### Pressure Dependence

Since a large number of investigations for unalloyed titanium are well correlated by Equation (23), it is possible to discern if  $K_O$  is dependent on oxygen pressure. Table 4-1 below lists the oxygen pressures considered. We conclude that there is no dependence of oxidation rate on oxygen pressure in the range of conditions under consideration. Wolf (10) obtained one data point at 400 torr for which  $K_p$  was about twice the value be obtained at 200 torr and the same temperature. He thus claims that "the degree of reaction is very nearly linearly related to oxygen pressure. This speaks strongly against any type of solid-state reaction control..". It seems quite unwarranted for Wolf to make such a claim based on one data point, when there is so much evidence in the literature to the contrary: we are of the opinion that Wolf's result should be disregarded at this time.

Table 4-1. Oxygen Pressures in Investigations of Unalloyed Titanium

<u>INVESTIGATION</u>	<u>PRESSURES</u>
Wolf (10)	200 torr
Stringer (21)	1 atm
Kofstad et al. (14)	1 atm
Jenkins (22)	40-700 mm
Davies and Birchenall (23)	1 atm
Hurlen (24)	1-760 mm

### Ti-6Al-4V Alloy

The only data available for this alloy is that of Wolf (10), which is also shown in Figure 4-5. The oxidation rate is higher than that for unalloyed titanium which is in line with the conclusion of Shambler and Redden (15) that  $\bar{v}_2$  increases somewhat with substitutional alloying content. Given the scatter in the experimental data there is no basis for concluding that the activation energy differs from that of unalloyed titanium. For temperatures above 1000 C Equation (23) can be approximated

$$4K_O^2 \approx 320 \exp \left( - \frac{61,800}{RT} \right) \text{ gm}^2/\text{cm}^2\text{s} \quad (\text{unalloyed}) \quad (24)$$

For Ti-6Al-4V the values of  $K_O^2$  measured were on an average 60% higher than Equation (23), thus we recommend

$$4K_O^2 = 480 \exp \left( - \frac{61,800}{RT} \right) \text{ gm}^2/\text{cm}^2\text{s} \quad (\text{Ti-6Al-4V}) \quad (25)$$

#### 4.1.3 Oxidation of Titanium by Steam

At the temperatures and pressures of interest steam will be only slightly dissociated. Table 4-2 below tabulates equilibrium compositions at 0.3 atm pressure.

Table 4-2. Equilibrium Compositions of Steam at 0.3 atm (25).

COMPOSITION (MOLE FRACTIONS)	TEMPERATURE <sup>0</sup> K			
	1200	1400	1500	1700
H <sub>2</sub>	0	.0001	.0003	.0007
H <sub>2</sub> O	1.0000	.9998	.9995	.0089
O <sub>2</sub>	0	0	.0001	.0003
OH	0	0	.0001	.0002



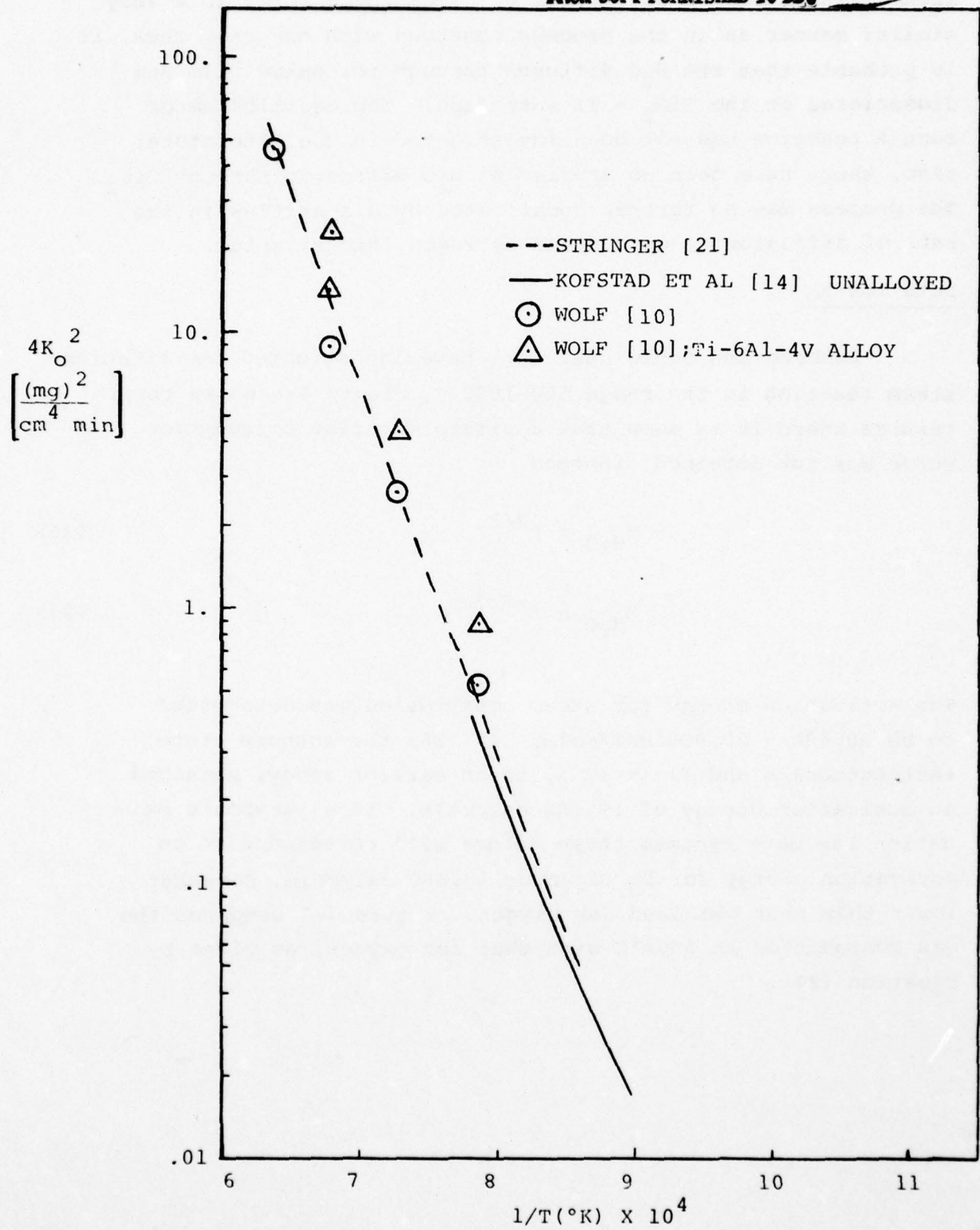


FIGURE 4-5. OXIDATION RATE CONSTANT FOR TI-6AL-4V

When titanium reacts with steam an oxide layer forms in a very similar manner as in the process observed with oxygen; thus, it is probable that the  $H_2O$  diffuses through the oxide film and dissociates at the  $TiO_2 - Ti$  interface. The equilibrium of such a reaction has not been investigated in the literature; also, there have been no studies of  $H_2O$  diffusion through  $TiO_2$ . The process may be further complicated by disparities in the rate of diffusion of oxygen and hydrogen into titanium.

#### Data for $K_O$

Löhberg and Schleicher (26) have investigated the titanium-steam reaction in the range 600-1000 C. Figure 4-6 shows their results where it is seen that a parabolic steam consumption curve was not obtained, instead

$$M_{H_2O} \propto t^{2/3} \quad (26)$$

$$\dot{M}_{H_2O} \propto t^{-1/3} \quad (27)$$

The activation energy for steam consumption was determined to be 20,400 - 20,900 cal/mole. In (26) the authors state that Lutschkin and Iljin (27), in an earlier study, obtained an activation energy of 19,100 cal/mole. If a parabolic oxidation law were assumed these values will correspond to an activation energy for  $\mathcal{D}_2$  of about 40,000 cal/mole, somewhat lower than that obtained for oxygen. Figure 4-7 compares the gas consumption at 1000°C with that for oxygen, as given by Equation (24).

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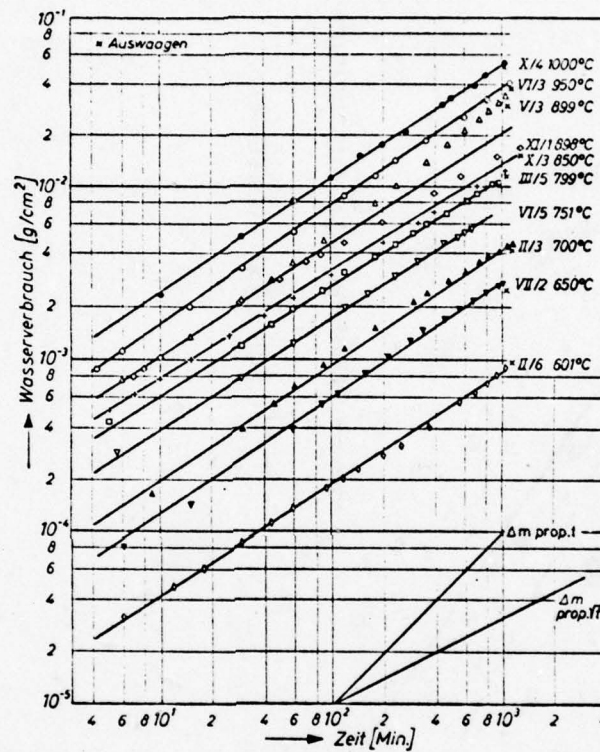


FIGURE 4-6. TITANIUM STEAM REACTION  
LÖHBERG AND SCHLEICHER



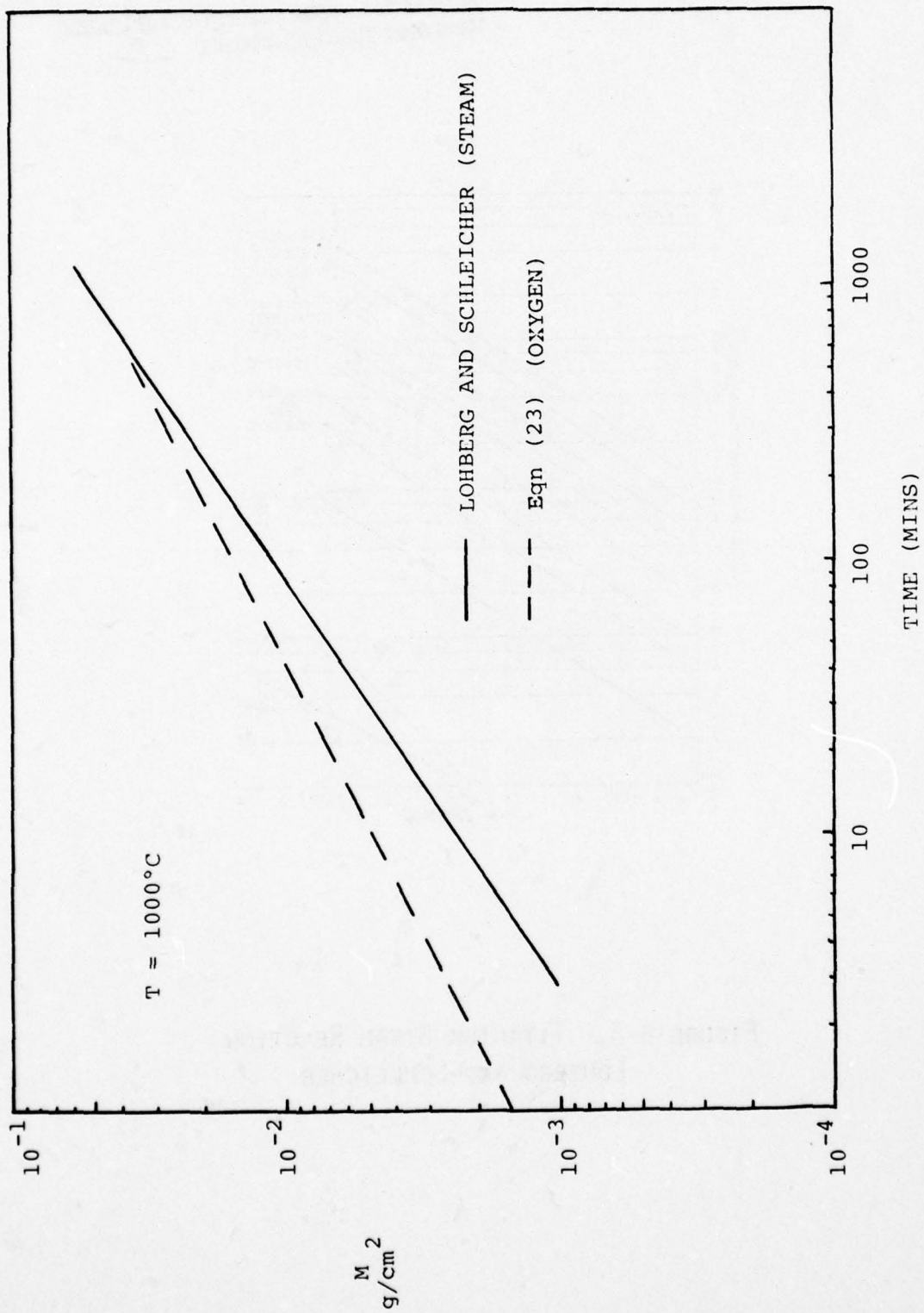


FIGURE 4-7. COMPARISON OF OXYGEN AND STEAM GAS CONSUMPTION

Lainer, Bai and Typsin (28) also studied the titanium-steam reactions but the data reported is sparse. Oxidation rates were correlated with the diffusion coefficient  $D_1$  for oxygen transport in a rutile scale. Values for  $D_1$  formed by oxidation in  $H_2O$  are claimed to be 40-600 times the values obtained for oxidation in air. No rate constants for the titanium-steam reaction are reported.

#### 4.1.4 Heats of Oxidation and Solution of Oxygen in Titanium

The energy evolved per gm atom of reacting oxygen in titanium for different end products has been calculated by Mah et.al. (Bureau of Mines Report of Investigation 5316) and is shown in Figure 4-8. For modeling purposes, it is adequate to use as heats of oxidation and solution, 12024 Btu/lb  $O_2$  and 15,575 Btu/lb  $O_2$  respectively.

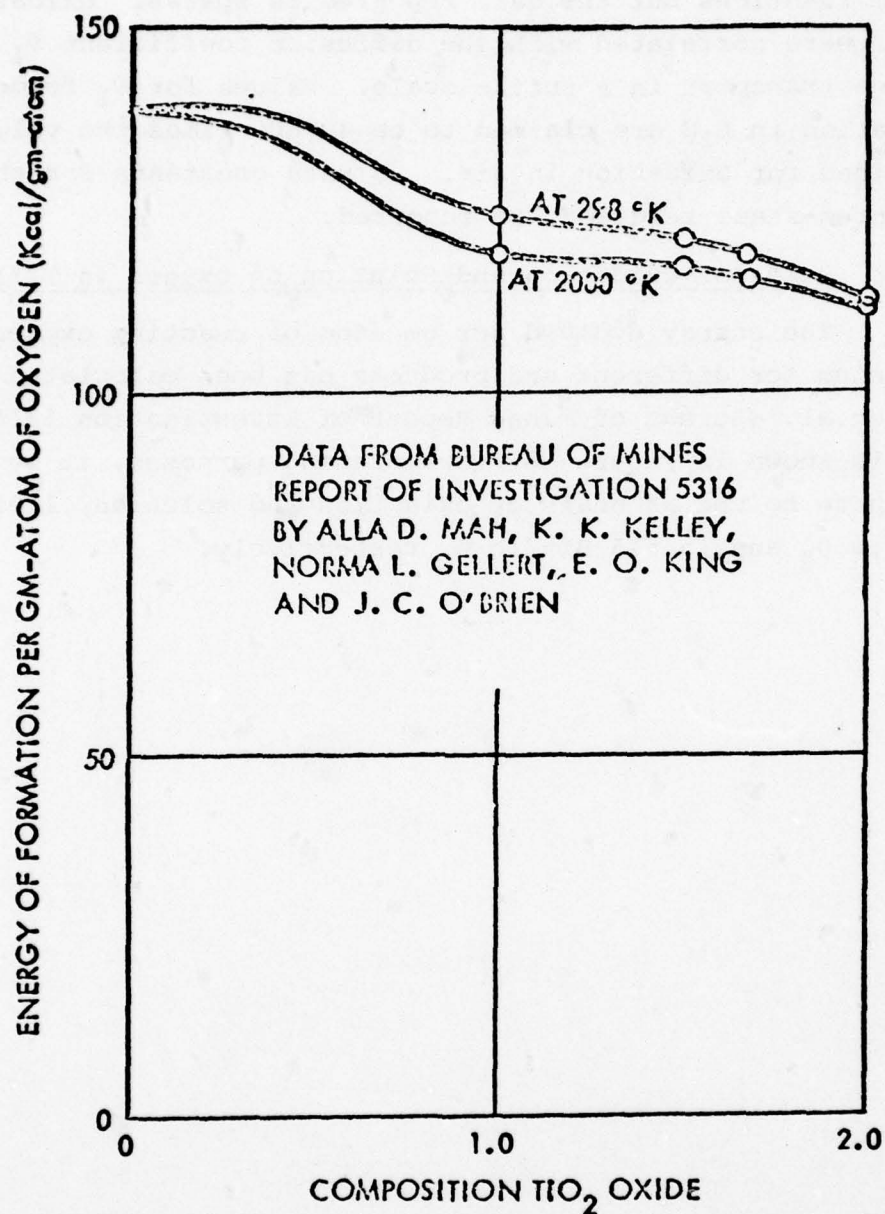


FIGURE 4-8. ENERGY PRODUCED PER GM-ATOM OF REACTING OXYGEN  
(16 GM O) IN TI FOR DIFFERENT END PRODUCTS  
AND REACTION TEMPERATURE



#### 4.1.5 Hydrogen Dissolution in Titanium Review

##### 4.1.5.1 Literature Survey

The dissolution of hydrogen in titanium differs from oxygen dissolution in that it is a reversible reaction, and provided the temperature is high enough to permit finite rate processes, titanium-hydrogen alloys can only exist in equilibrium with a gaseous hydrogen atmosphere. Figure 4-9 shows the equilibrium concentrations for pure titanium. Figure 4-10 shows the phase diagram and Figure 4-11 is deduced from 4-10.

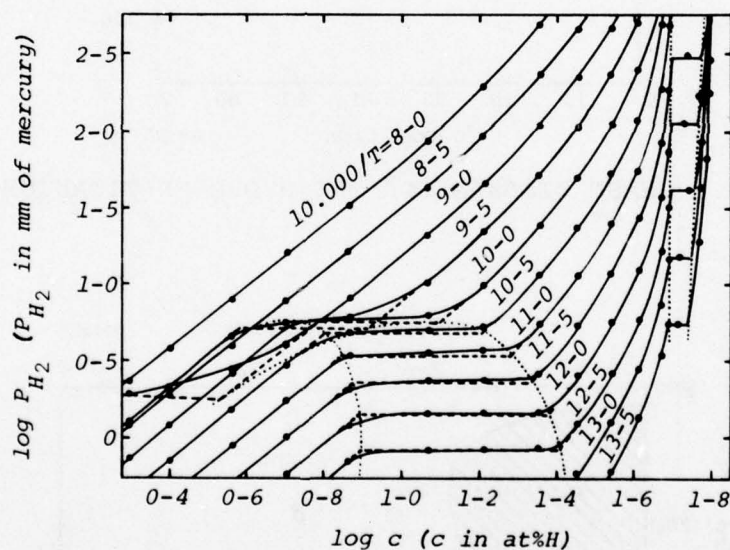


FIGURE 4-9. EQUILIBRIUM CONCENTRATIONS FOR PURE TITANIUM

Waisman, Sines and Robinson (29) investigated equilibrium for Ti-6Al-4V alloy and found that, at a given solid phase hydrogen concentration and temperature, the equilibrium gas pressure was 2.31 times that for pure titanium.

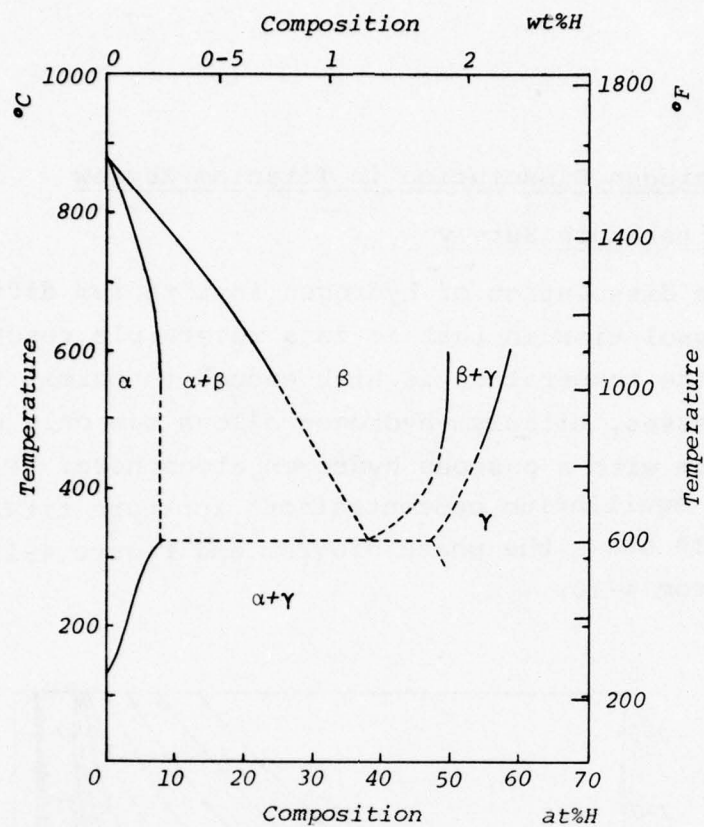


FIGURE 4-10. PHASE DIAGRAM FOR THE HYDROGEN-TITANIUM SYSTEM

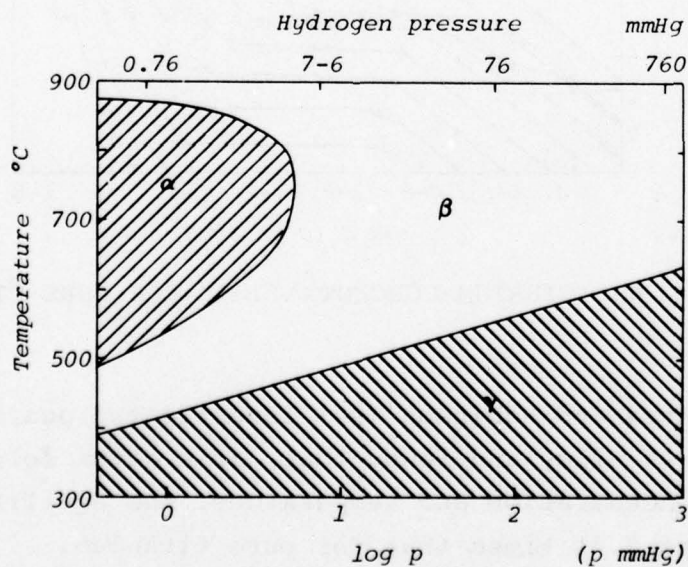


FIGURE 4-11. TITANIUM PHASES AS THEY DEPEND ON TEMPERATURE AND HYDROGEN PRESSURE

Diffusion coefficients of hydrogen in pure titanium have been measured by Wasilewski and Kehl (30) as

$$D_{\beta} = 1.95 \times 10^{-3} \exp \{(-6640+500)/RT\} \text{ cm}^2/\text{s}$$

$$D_{\alpha} = 1.8 \times 10^{-2} \exp \{(-12380+680)/RT\} \text{ cm}^2/\text{s}$$

which are considerably larger than the diffusion coefficients for oxygen in titanium.

The heat of solution of hydrogen in titanium has been calculated by McQuillan, and is reported by Skinner et.al. (31) as -21,600 cal/mole to form  $\alpha$  solution and -27,800 cal/mole to form  $\beta$  solution. These values are valid for dilute solutions (less than 10 atom % H).

#### 4.1.5.2 Sample Numerical Calculations

Since the mechanism and equilibrium of the titanium-steam reaction is unknown, it is only possible to obtain rough estimates of hydrogen dissolution in titanium exposed to steam. Since the diffusion coefficient for hydrogen in titanium is considerably larger than that for oxygen, a possible approach is to simply assume that the hydrogen goes into solution in the stoichiometric proportion indicated by the  $\text{H}_2\text{O}$  formula, i.e., 1 lb H for 8 lbs  $\text{O}_2$ . At 1200K the oxygen reaction rate is

$$\begin{aligned} \dot{M}_{\text{O}_2} &= K_{\text{O}} t^{-1/2} & K_{\text{O}} &= (4K_p)^{1/2} \\ & & &= 22.4 \exp \left( \frac{-30,900}{(1.987)(1200)} \right) \\ & & &= 5.27 \times 10^{-5} \text{ lb/ft}^2 \text{ s}^{1/2} \end{aligned}$$

$$\dot{M}_{\text{O}_2} = 5.27 \times 10^{-5} t^{-1/2} \text{ lb/ft}^2 \text{ s}^{1/2}$$



$$\begin{aligned}
 \text{Heat evolved} &= \dot{M}_{O_2} \Delta H \\
 &= (5.27 \times 10^{-5}) \left( \frac{280,000}{32} \right) (1.8) t^{-1/2} \\
 &= 0.83 t^{-1/2} \text{ Btu/ft}^2 \text{ s}^{1/2}
 \end{aligned}$$

Then

$$\begin{aligned}
 \dot{M}_{H_2} &= 0.125 \dot{M}_{O_2} \\
 &= 0.659 \times 10^{-5} t^{-1/2} \text{ lb/ft}^2 \text{ s}^{1/2}
 \end{aligned}$$

$$\begin{aligned}
 \text{Heat evolved} &= \dot{M}_{H_2} \Delta H \\
 &= (0.659 \times 10^{-5}) \left( \frac{27,800}{2} \right) (1.8) t^{-1/2} \\
 &= 0.165 t^{-1/2} \text{ Btu/ft}^2 \text{ s}^{1/2}
 \end{aligned}$$

which is about 20% of the heat evolved by the  $O_2$  reaction.

However, McQuillan (32) states that the rate of hydrogen absorption is considerably reduced when the surface has been "contaminated" by oxygen. No quantitative information on the effect has been published, but Gulbransen and Andrew (33) have examined the corresponding effect in Zirconium in some detail. A further and, perhaps, more important consideration is that the bulk of the water vapor available for reaction with a titanium shroud results from evaporation of water droplets or ice particles. Let us now calculate the latent heat associated with a droplet evaporation process to produce the hydrogen dissolution rate calculated above. The amount of water evaporated to sustain the hydrogen dissolution rate calculated above is

$$\begin{aligned}\dot{M}_{H_2} &= (81/2)\dot{M}_{H_2} = (18/2) (.659 \times 10^{-5})t^{-\frac{1}{2}} \\ &= 5.93 \times 10^{-5}t^{-\frac{1}{2}} \text{ lb/ft}^2\text{s}^{\frac{1}{2}}\end{aligned}$$

and since the latent heat is approximately 1000 Btu/lb the rate at which heat is absorbed is

$$Q_{\text{vap}} = (5.93 \times 10^{-5})(1000)t^{-\frac{1}{2}} = .059t^{-\frac{1}{2}} \text{ Btu/ft}^2$$

which is 36% of the heat evolved by the hydrogen dissolution. Thus, at most the net increase in heat liberation is  $(1 - 0.36)(20) = 12.8\%$  more than the value obtained for oxidation in air or oxygen.

#### 4.1.5.3 Effect of Temperature Level

At higher temperatures the degree of dissociation of  $H_2O$  will be greater (see Table 4-2), and the diffusion coefficient of H in titanium is also higher; however, the solubility of H decreases rapidly with temperature (see Figure 4-9) and the net effect is, for example, at 1500K the rate of dissolution of H is about 40% less than at 1200K.

#### 4.1.6 Evaluation of Clemson Data (3) for Oxygen Consumption Rate: Ti-6Al-4V Alloy

##### 4.1.6.1 Model Parameters Based on Weight Change Measurements

Based on the long time weight change measurements made at Clemson (10) we proposed Eq. (24) to give the rate constant  $K_p$  for oxidation of Ti-6Al-4V alloy, viz.

$$K_p^2 = 480 \exp \left( \frac{-61,800}{RT} \right) \text{ gm}^2/\text{cm}^2\text{s} \quad (24)$$

Our model parameters  $D_1$ ,  $D_2$ ,  $\gamma$  and  $K_O$  be calculated from  $K_p$  as follows. Ignoring moving boundary effects and postulating 80% of the oxygen goes into solution while 20% goes to form oxide, we can derive

$$4K_O^2 = K_p^2 \quad (25)$$

$$\frac{\rho_{\text{TiO}_2}}{3.33} D_1^{1/2} \gamma^2 + C_u \left( \frac{D_2}{\pi} \right)^{1/2} \gamma - \frac{D_1^{1/2}}{2} (C_a - C_s) = 0 \quad (26)$$

$$2C_u \left( \frac{D_2}{\pi} \right)^{1/2} t^{1/2} = (0.8) (4K_O^2)^{1/2} t^{1/2} \quad (27)$$

$$2C_u \left( \frac{D_2}{\pi} \right)^{1/2} t^{1/2} = 4 \left( \frac{C_a + C_s}{2} \right) \gamma (D_1 t)^{1/2} \quad (28)$$

with  $C_u = 40.2 \text{ lb/ft}^3$

$$C_s = 106.3 \text{ lb/ft}^3$$

$$C_a = 107.2 \text{ lb/ft}^3$$

$$\rho_{\text{TiO}_2} = 281 \text{ lb/ft}^3$$

and assuming the same activation energy for  $D_1$  and  $D_2$ , the equations may be solved to give



$$\gamma = .0297$$

$$D_{10} = 2.03 \text{ ft}^2/\text{s}$$

$$D_{20} = 0.676 \text{ ft}^2/\text{s}$$

#### 4.1.6.2 Comparison with Volumetric O<sub>2</sub> Consumption Measurements

Table 4-3 summarizes the pertinent details of the tests for which satisfactory measurements of oxygen consumption rate were made. Turning first to the low heating rate tests (0.5°C/s), Figure 4-12 shows a comparison of the predictions of our computer code with the experimental data for  $\dot{M}_{O_2}$  as a function of time. Since the prediction lies between the experimental results for the two types of Ti-6Al-4V alloy, we view the prediction as quite satisfactory. For these low heating rates, Wolf et.al. (34) also concluded that the parabolic kinetics implicit in the model are satisfactory.

Figure 4-13 shows a comparison at a heating rate of 8°C/s where the comparison is, at first sight, less satisfactory. However, a number of considerations are pertinent. (i) In the Clemson experiments, there were apparent difficulties in recording the zero time point accurately. Table 3 compares the time that should have elapsed to reach 1100°C (calculated) with the actual time; the discrepancies are 40, 45 and 30 seconds for the three specimens. Thus, in Figure 13 the experimental curves have been adjusted by the above time displacements, a rather unsatisfactory procedure. (ii) Since the three specimens are of the same type of Ti-6Al-4V alloy, the differences between the experimental curves indicate the lack of precision in the experiments and possible variability of physical phenomena (e.g., cracking of the oxide scale). (iii) The data points indicated on the

TABLE 4-3. SUMMARY OF SPECIMENS (Ti6AL-4V) USED TO COMPARE PREDICTED REACTION RATE WITH EXPERIMENT (10)

Specimen No.	Type	Final Temp. °C	Heating Rate °C/s	Calculated Time to 1100°C (sec)	Actual Time to 1100°C (sec)	Actual Time to $\dot{M}_{max}$ (sec)
401161	1	1100	0.5	2150	2280	2190
402042	2	1100	0.5	2150	2220	2070
405071	1	1100	8	134.4	174.0	174.0
405072	1	1100	8	134.4	180.0	192.0
11202	1	1100	8	134.4	165.0	135.0
402043	2	1100	22	48.9	67.8	60.0
401092	1	1100	22	48.9	81.0	45.0

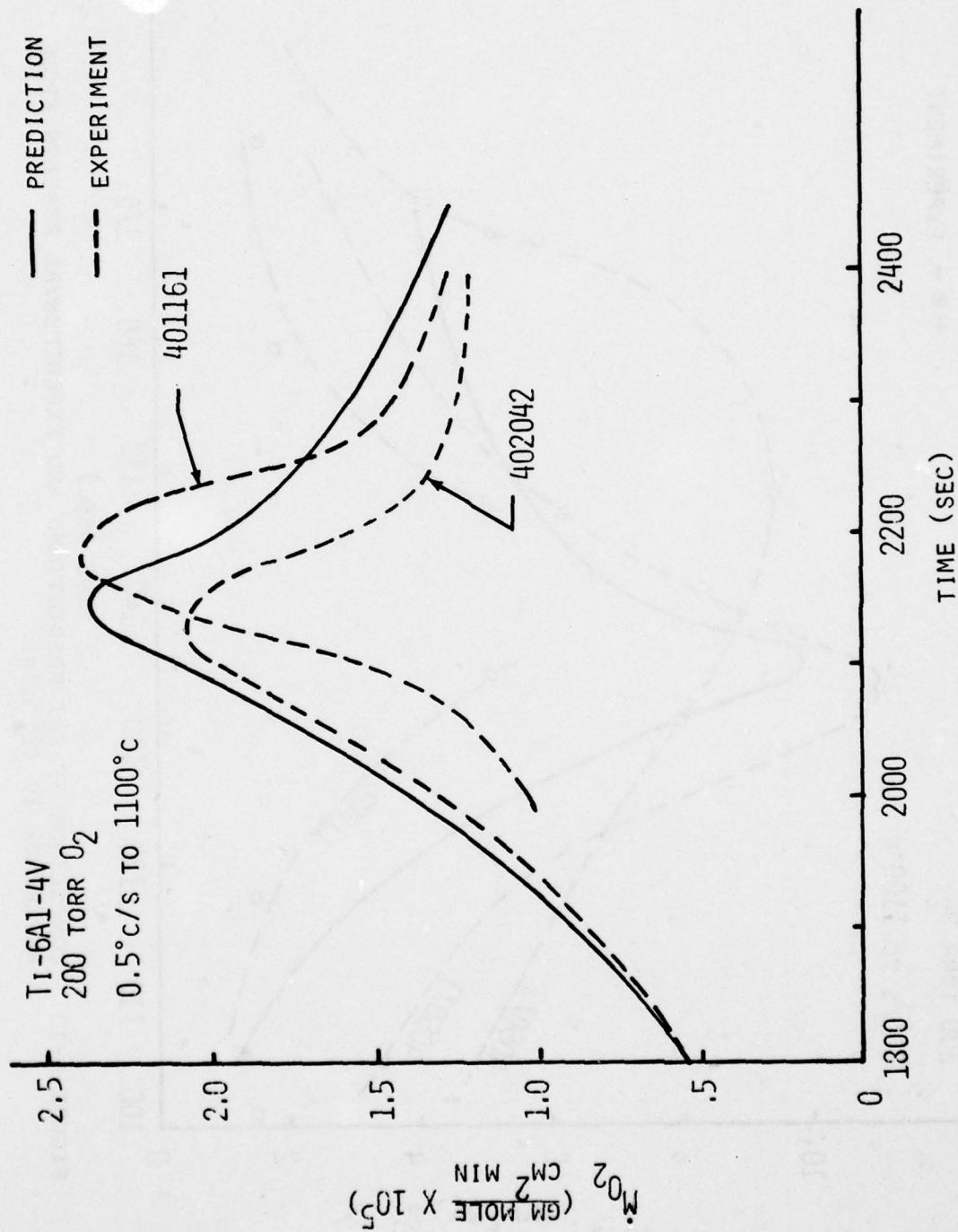


FIGURE 4-12. COMPARISON OF SAI PREDICTIONS AND EXPERIMENTAL RESULTS FROM  
 REFERENCE 10 (0.5°C/s)



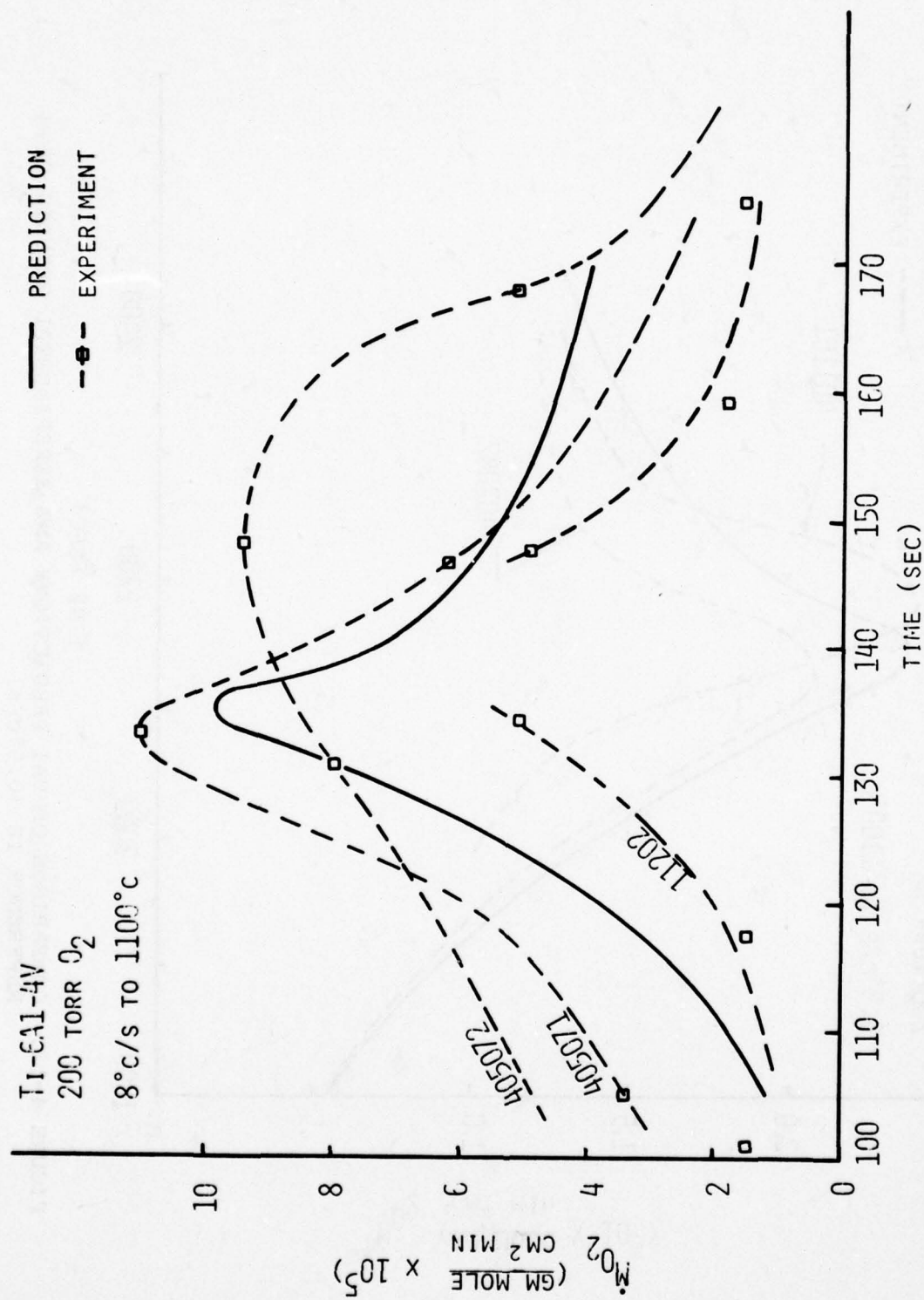


FIGURE 4-13. COMPARISON OF SAI PREDICTIONS AND EXPERIMENTAL RESULTS FROM REFERENCE 10 (8° c/s)

experimental curves are those actually recorded. It is clear that they are too sparse to record a peak in  $\dot{M}_{O_2}$  as sharp as indicated by theory. Furthermore, in the experiments there were problems in preventing temperature overshoots at the end of the heating period. Such overshoots would tend to broaden the observed peaks in  $\dot{M}_{O_2}$ . Figure 4-14 shows a comparison at a heating rate of  $22^\circ\text{C/s}$ ; again, the sharpness of the predicted peak in  $\dot{M}_{O_2}$  is in evidence.

In our review, the predictions at higher heating rates are adequate in view of the experimental uncertainties. Thus, we do not support the view of Wolf et.al. (34) that at high heating rates the parabolic kinetics should be discarded in favor of the asymptotic rate law of Evans (35). Furthermore, we are also doubtful if further corrections should be made as suggested in (10), for example, the suggested increase in effective reaction surface area during rapid heating. It is important to note that the introduction of an ad hoc kinetics expression such as the asymptotic rate law would preclude rational modeling of the oxidation process: it would then not be possible to account for such features as spatial temperature variations, and mechanical removal of the oxide film.

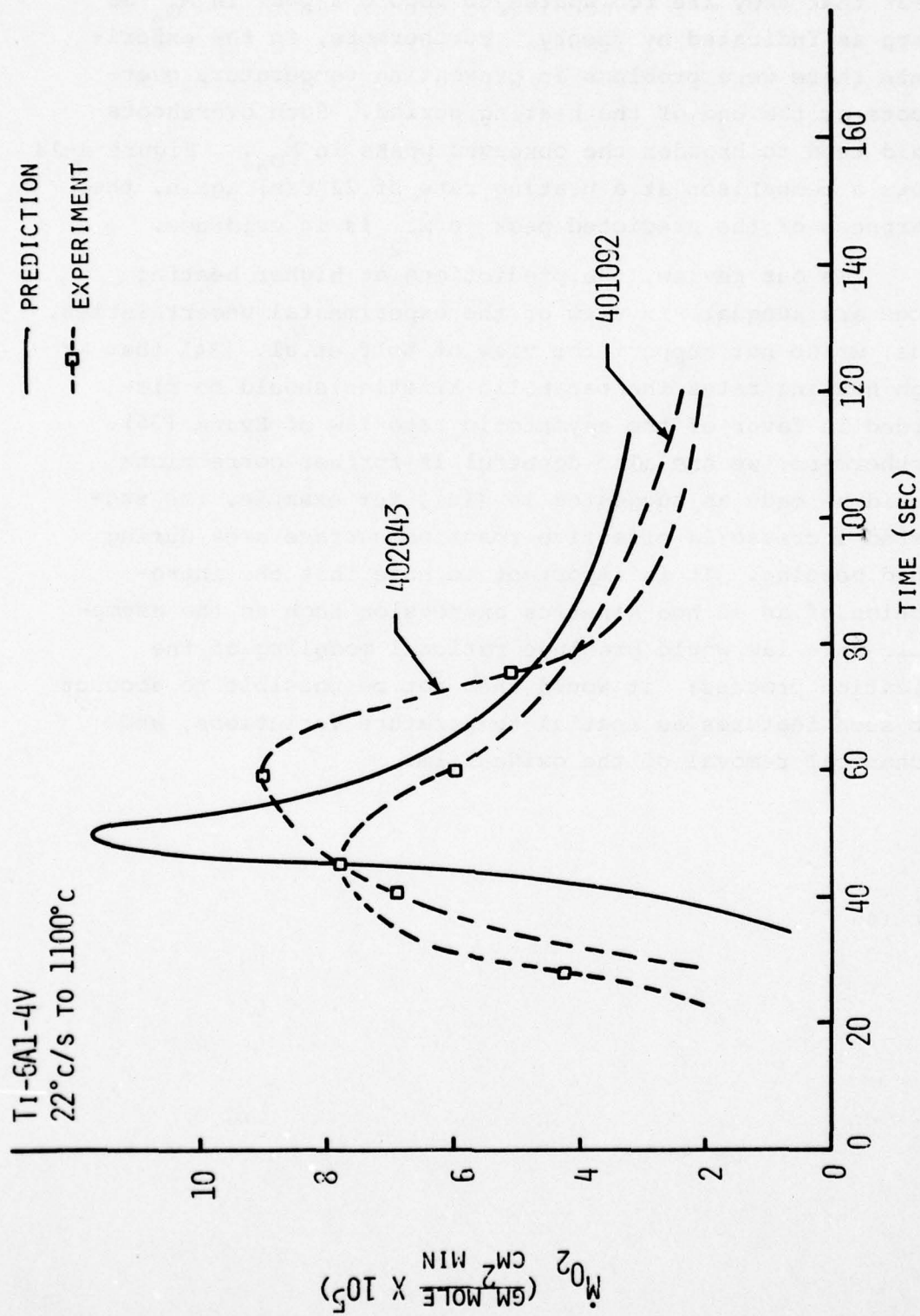


FIGURE 4-14. COMPARISON OF SAI PREDICTIONS AND EXPERIMENTAL RESULTS FROM REFERENCE 10 (22° c/s)



#### 4.2 Analysis of Oxidation Test Data

The analytical model developed in Section 4.1 for oxidation of 6AL-4V titanium in oxygen environments was used to analyze the results of the Phase I SAI oxidation test data. Analytical predictions for the weight gain as a function of time for the indicated experimentally measured temperature history are shown in Figure 4-15 for typical runs. The final experimental weight gain is shown for comparison.

Important conclusions from this analysis include:

- 1) weight gain during the transient heat-up period is not important
- 2) the tests were essentially isothermal temperature oxidation governed by the parabolic law as developed in Section 4.1.

The total experimental data base is shown in Figure 4-16 in terms of weight gain ( $\Delta W$ ) normalized by square root of time (reflecting the parabolic law) in comparison with the analytical model and uncertainty bands based on information in the literature. The Phase I SAI data falls within the uncertainty bounds of the model and generally supports the parabolic oxidation rate law. Within the context of this evaluation, an increased oxidation in  $H_2O$  vapor is shown up to 1700°K. A pressure effect is also apparent, especially at 1400°K, although the 1400°K data appear anomalous compared to the other data points.

Application of the oxidation model to the AEDC DET data shows good agreement with measured heat transfer. Figure 4-17 illustrates the Run 7 ti-22 model clear air response stagnation point heat transfer data in comparison with predictions. The dominant convective heating trend

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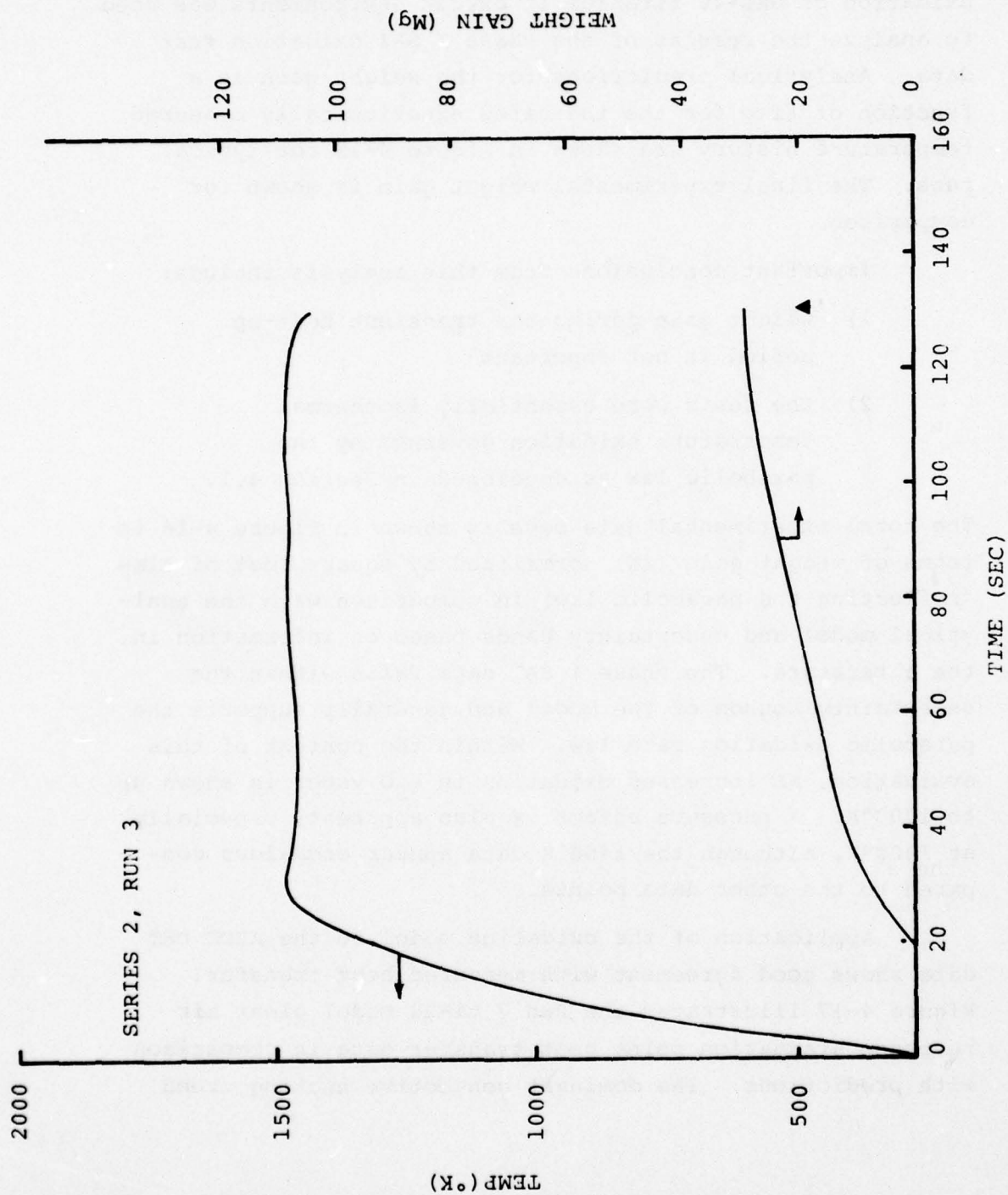


FIGURE 4-15A. ANALYSIS OF SAI OXIDATION DATA RUNS

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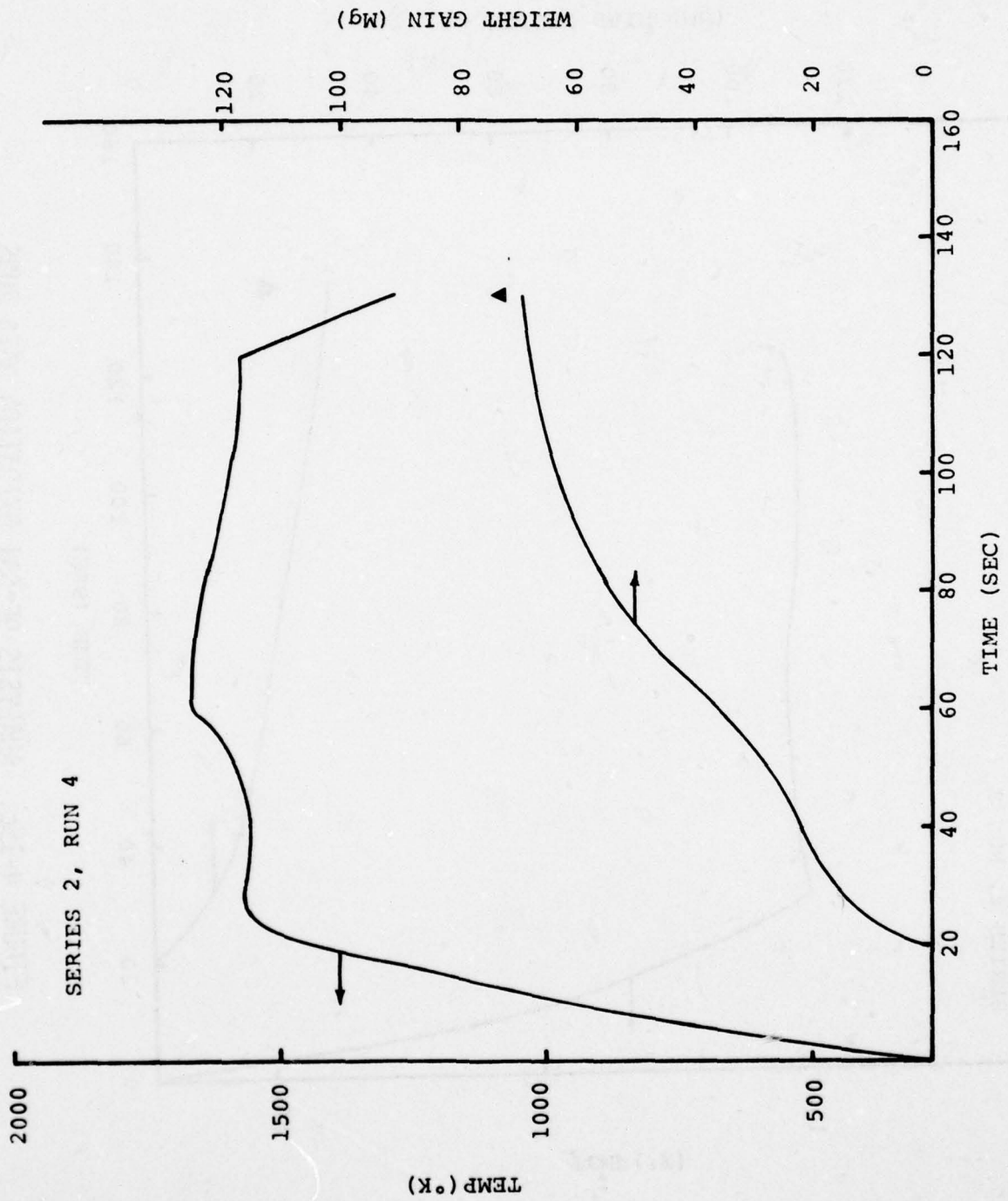


FIGURE 4-15B. ANALYSIS OF SAI OXIDATION DATA RUNS



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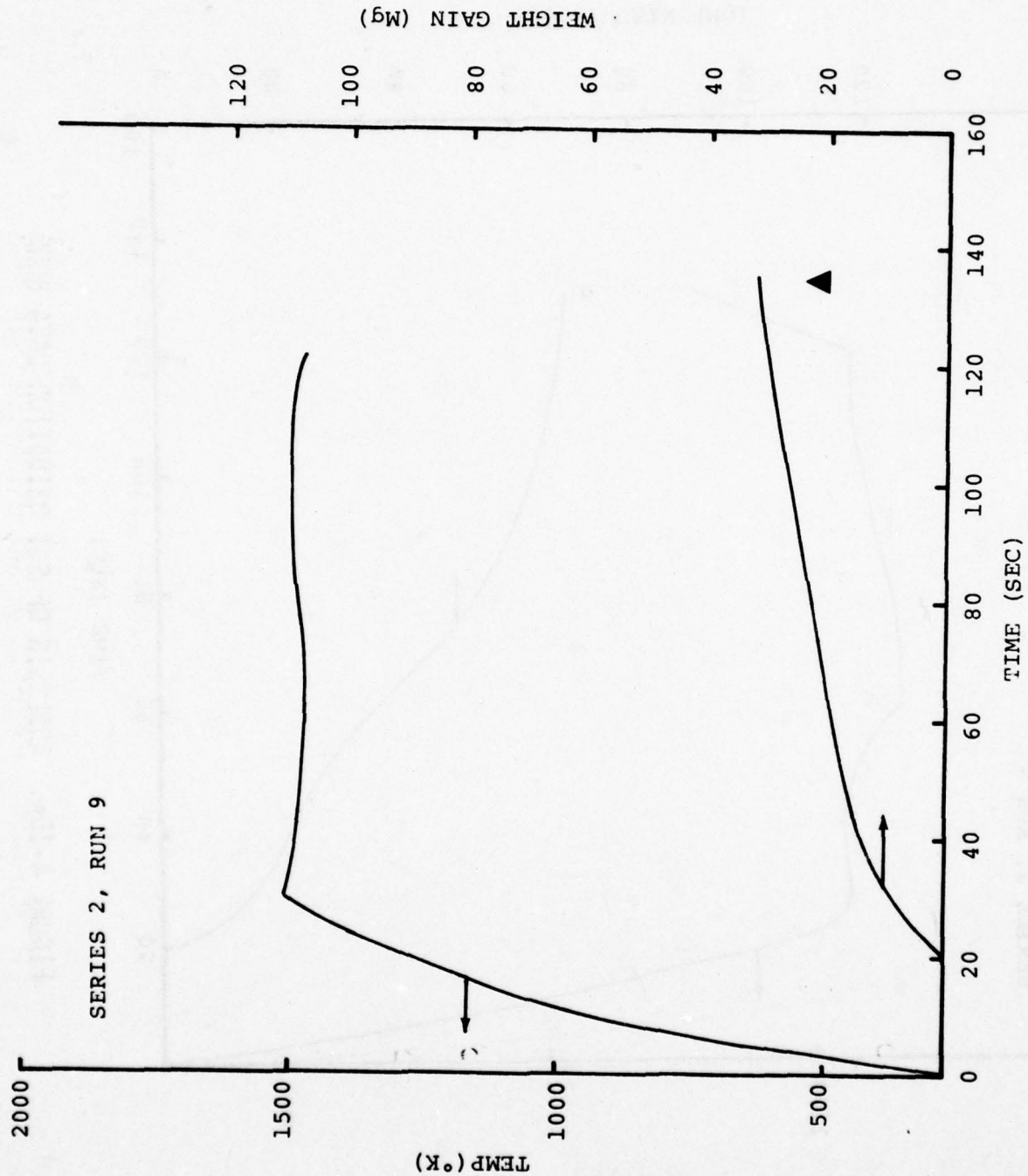


FIGURE 4-15c. ANALYSIS OF SAI OXIDATION DATA RUNS

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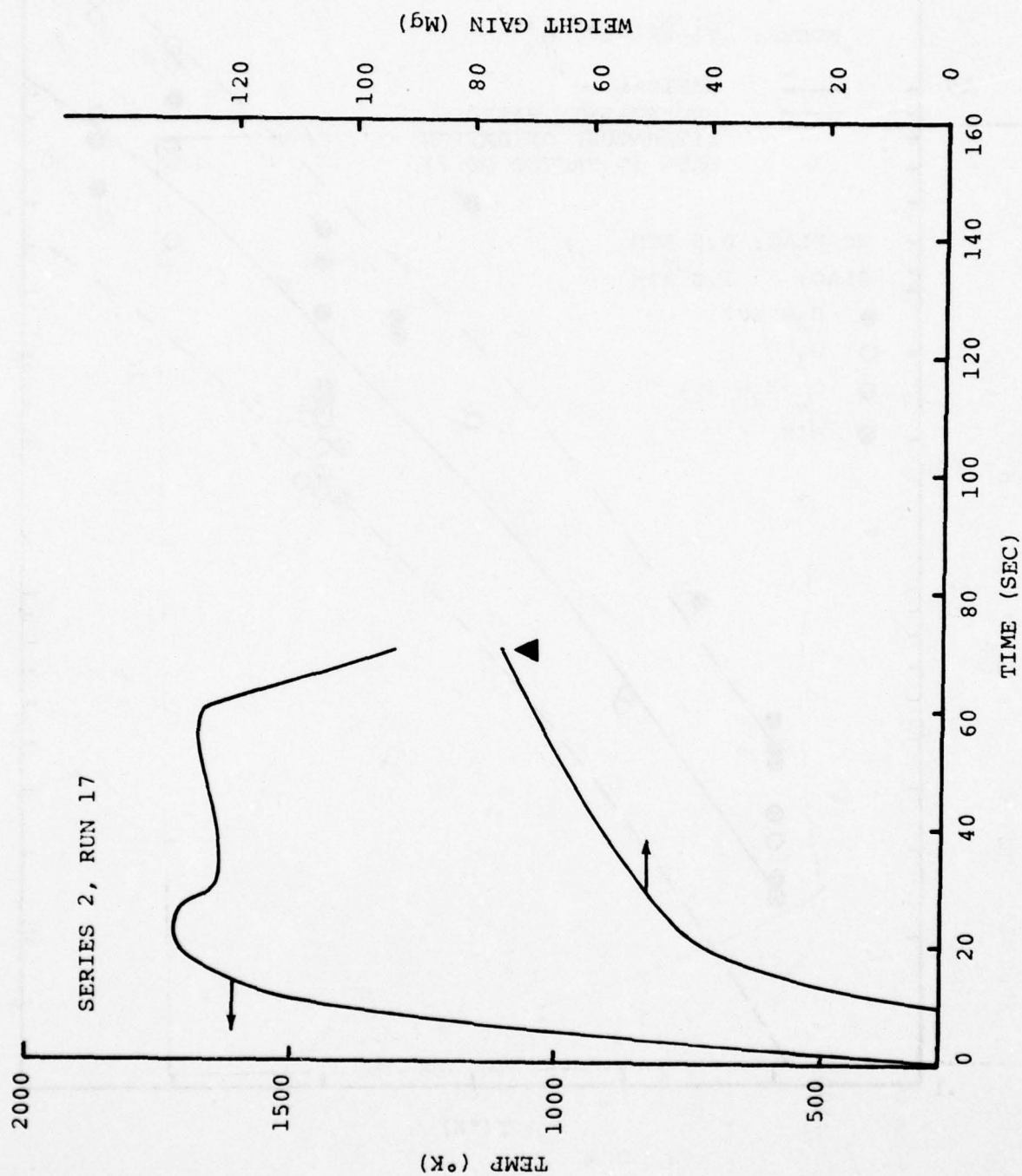


FIGURE 4-15D. ANALYSIS OF SAI OXIDATION DATA RUNS

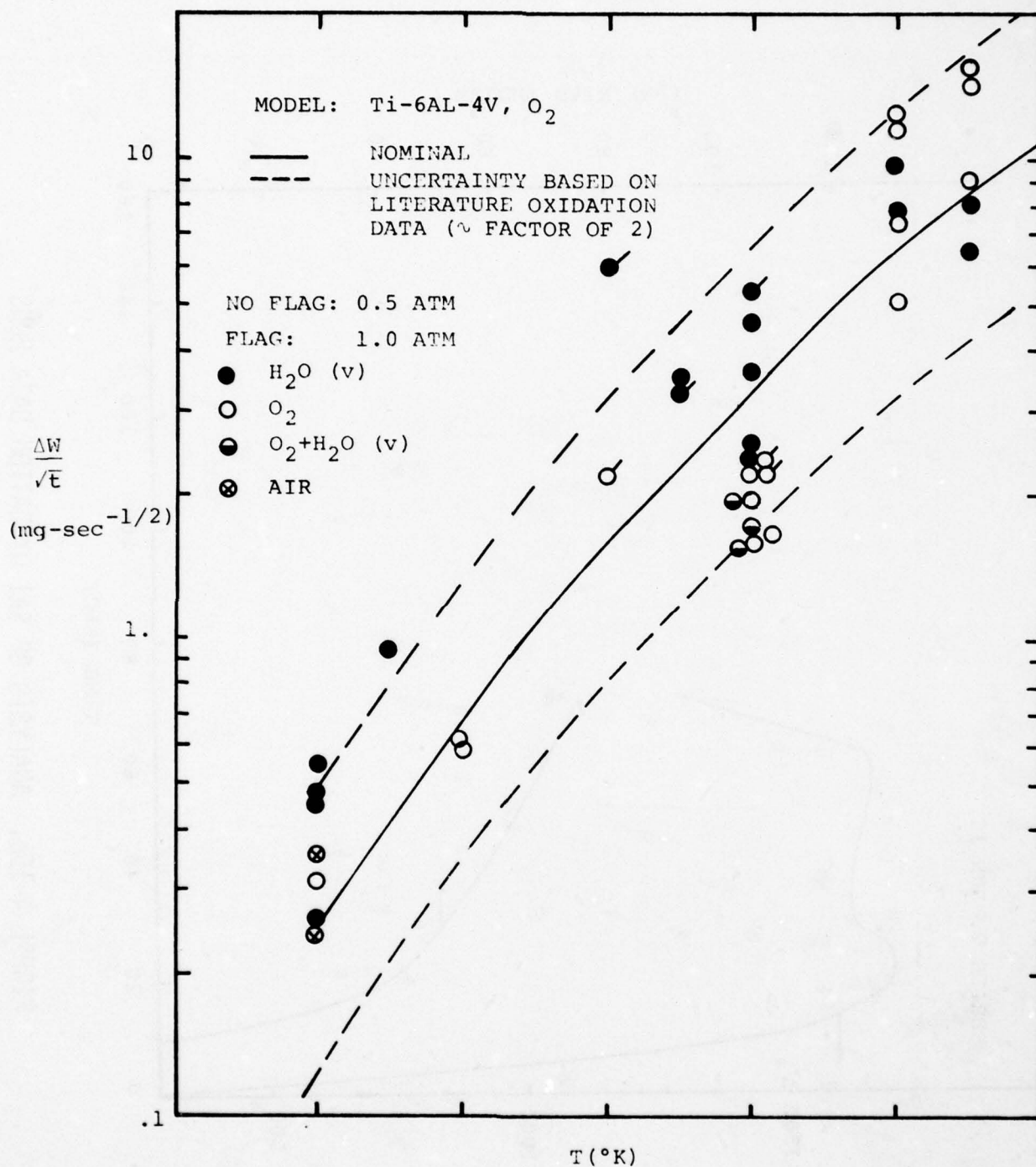


FIGURE 4-16. COMPARISON OF EXPERIMENTAL AND ANALYTICAL TITANIUM OXIDATION RESULTS



EXPERIMENTAL DATA FOR STAGNATION PT.

- ◇ 10 DEG TC #4
- 10 DEG TC #3
- △ 5 DEG TC #2
- 0 DEG TC #1

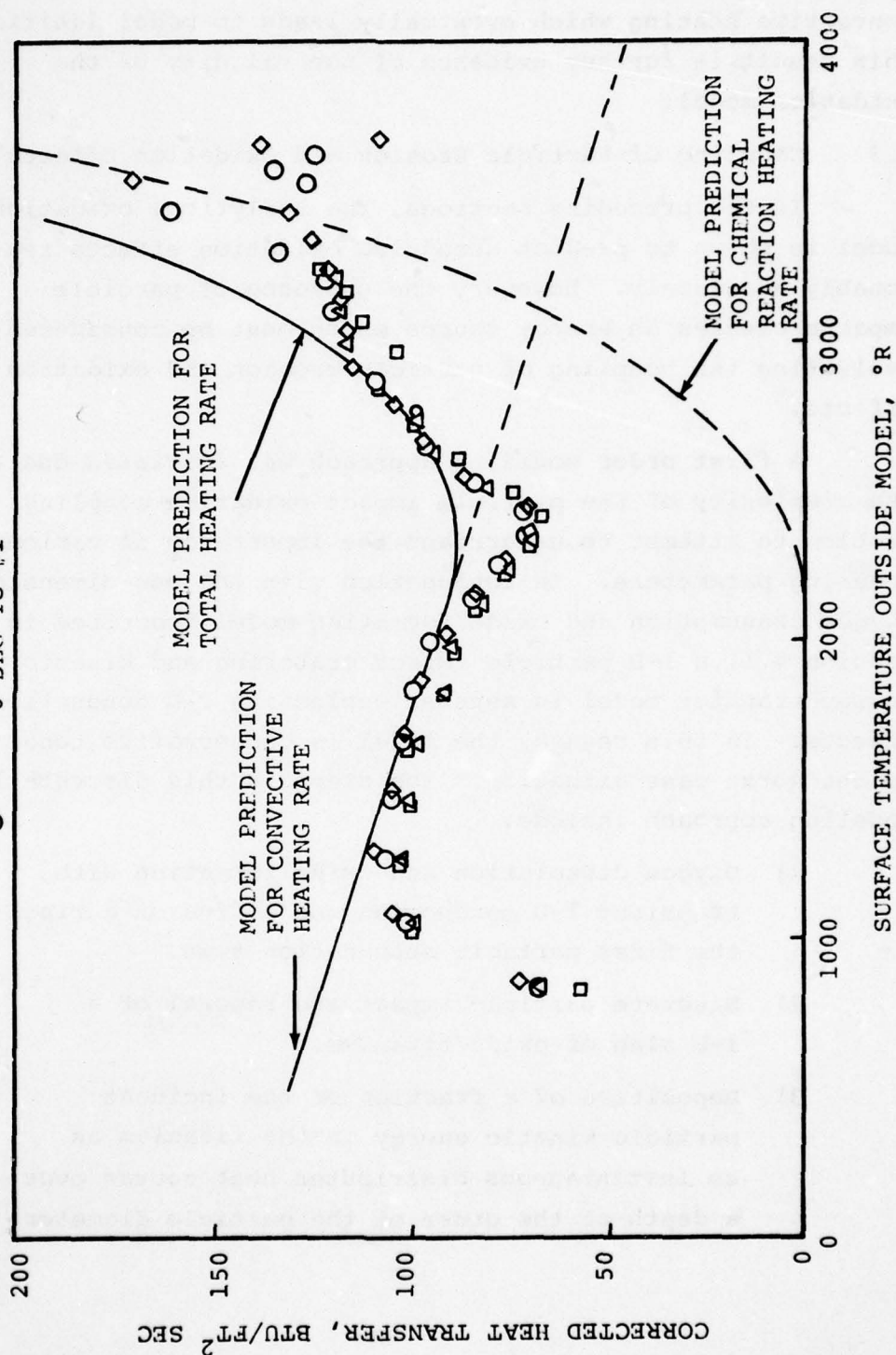


FIGURE 4-17. COMPARISON OF MODEL WITH EXPERIMENT FOR  
RUN 7, MODEL TI-22, CLEAR AIR

occurs until 2200°R where surface oxidation heating becomes evident. Above 3000°R, the chemistry effect exceeds the convective heating which eventually leads to model ignition. This result is further evidence of the validity of the oxidation model.

#### 4.3 Coupling of Particle Erosion and Oxidation Effects

In the preceding sections, the analytical oxidation model is shown to predict uncoupled oxidation effects reasonably accurately. However, the presence of particle impacts creates an energy source which must be considered in evaluating the coupling of particle erosion and oxidation effects.

A first order modeling approach was initiated due to the complexity of the particle impact-oxidation coupling problem to attempt to understand the importance of various modeling parameters. In conjunction with the one-dimensional oxygen consumption and oxide formation model described in Section 4.1, a 1-D particle impact cratering and kinetic energy transfer model is assumed neglecting 2-D conduction effects. In this regard, the model is conservative tending to the worst case situation. The steps in this discrete 1-D modeling approach include:

- 1) Oxygen dissolution and oxide formation with transient 1-D conduction and diffusion during the first particle obscuration time.
- 2) Discrete particle impact and removal of a 1-D slab of oxide/titanium.
- 3) Deposition of a fraction of the incident particle kinetic energy in the titanium as an instantaneous distributed heat source over a depth of the order of the particle diameter.

- 4) Transient 1-D conduction and oxygen diffusion with oxide re-formation over the next particle obscuration time.

This discrete modeling approach results in local crater hot spots due to kinetic energy deposition followed by thermal diffusion (and thus crater cooling) over the time between impacts. When the bulk temperature reaches a critical level, a subsequent impact causes a local ignition due to the high local crater temperature and thus chemical heat release locally. During this latter phase, the solid phase oxidation and dissolution process becomes so large as to be gas phase diffusion-limited. Thus, the boundary layer transfer processes also become coupled to the overall solid phase oxidation process.

It must be emphasized that the model presented herein for this highly coupled particle erosion/oxidation ignition process is intended to identify the key features involved. In this respect, a number of adjustable parameters have been introduced relating to the details of the particle kinetic energy deposition process and to the gas phase diffusion limited oxidation rates.

The key parameters in this modeling include:

- $\rho_{p\infty} \equiv$  particle mass density
- $d_p \equiv$  particle diameter
- $V_p \equiv$  particle velocity
- $\delta \equiv$  titanium thickness
- $Q_{cw} \equiv$  cold wall convective heat transfer rate
- $H_r \equiv$  BL recovery enthalpy
- $\alpha_H \equiv$  depth of kinetic energy deposition as fraction of  $d_p$



TABLE 4-4. PARAMETERS FOR IMPACT-OXIDATION CALCULATION

Case	$\rho_{p\infty}$ (g/cc)	$d_p$ (mm)	$V_p$ (ft/sec)	$\delta$ (in.)	$Q_{cw^2}$ (Btu/ft <sup>2</sup> -sec)	Hr (Btu/lb)	$\alpha_H$ --	$\eta$ --	$\dot{m}_{O_2}$
1	$10^{-6}$	.1	6000	.1	100	500	1	1	1,2
2	$10^{-7}$	.1	6000	.1	100	500	1	1	1,2
3	$10^{-6}$	1	6000	.1	100	500	1	1	1,2
4	$10^{-6}$	1	6000	.2	100	500	1	1	1,2
5	$10^{-6}$	1	6000	.5	100	500	1	1	1,2

$\eta$   $\equiv$  fraction of particle kinetic energy  
transferred to thermal energy

$\dot{m}_{O_2}$   $\equiv$  augmented BL oxygen mass flux normalized  
by unaugmented value

Table 4-4 on the preceding page illustrates the representative values chosen for this parametric study. The results of the parametric calculations are shown in Figure 4-17. No local hot spot ignition is predicted except for case 3 with 1mm particles, 0.1 in. thick titanium, and an augmented BL oxygen mass flux by a factor of 2. For unaugmented mass flux, the problem is gas phase diffusion controlled which prevents an ignition in this case. Although case 3 predicts, qualitatively, ignition for larger particles, cases 4 and 5 illustrate that this can be alleviated using thicker titanium material. These results seem to indicate the importance of the gas phase oxygen mass flux diffusion limitations in preventing ignition at higher temperatures. The results also indicate an increased concern for ignition for higher dust densities and particle sizes, but ignition was not predicted for conditions of interest below approximately 2000°F bulk temperatures which still appears to be a reasonable design criteria.

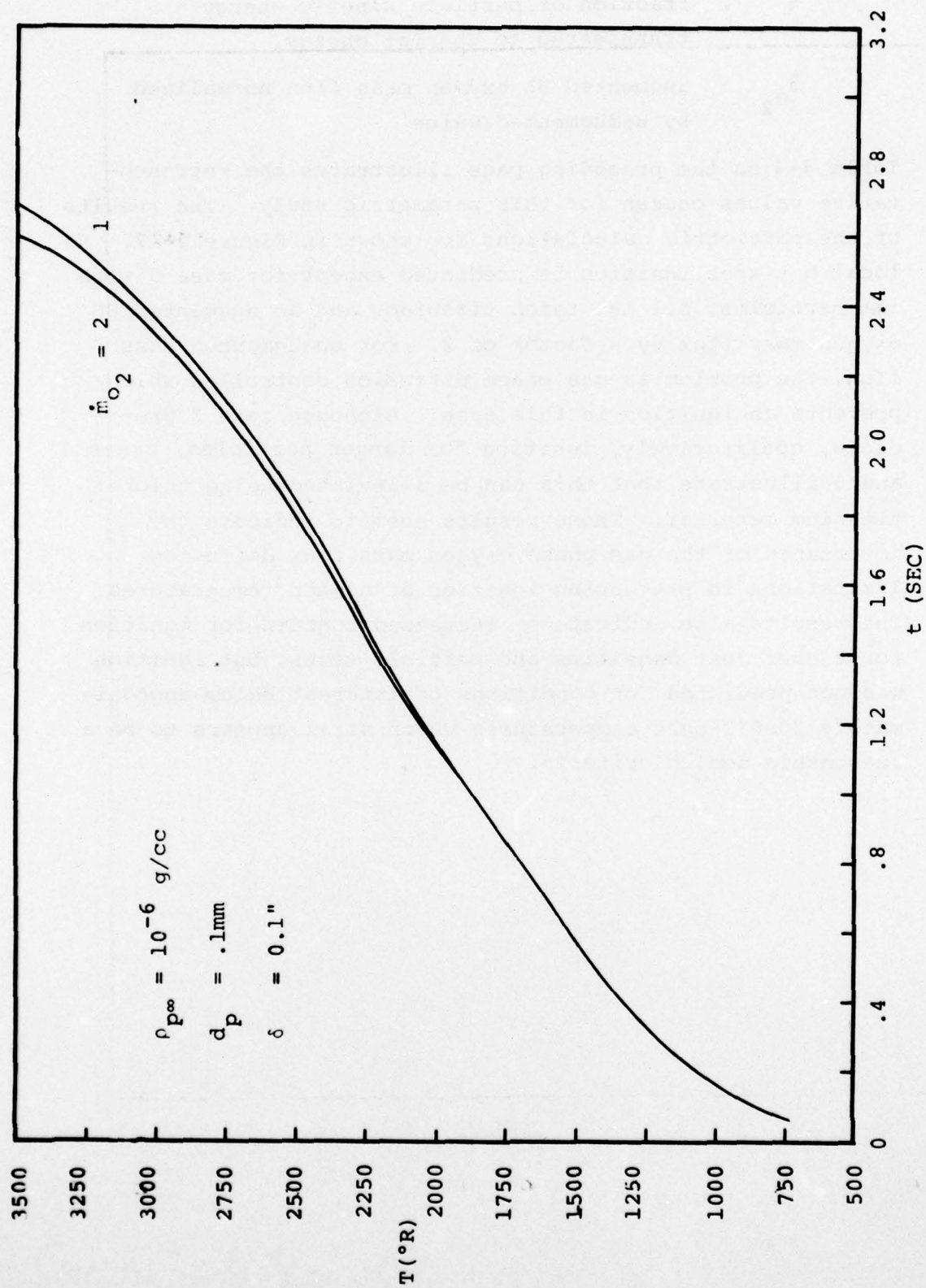


FIGURE 4-18A. TITANIUM RESPONSE TO PARTICLE IMPACT-OXIDATION



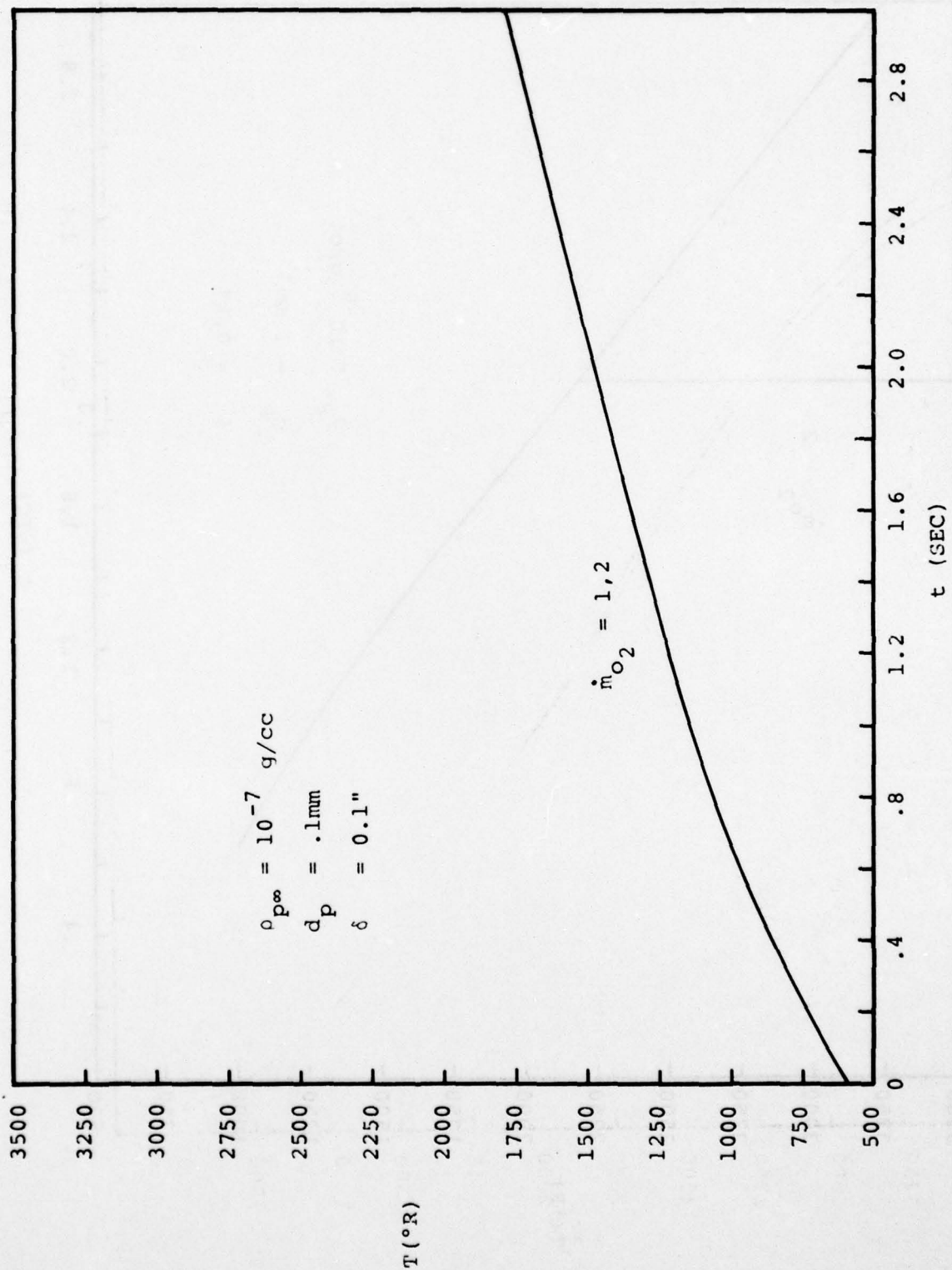


FIGURE 4-18A. TITANIUM RESPONSE TO PARTICLE IMPACT-OXIDATION

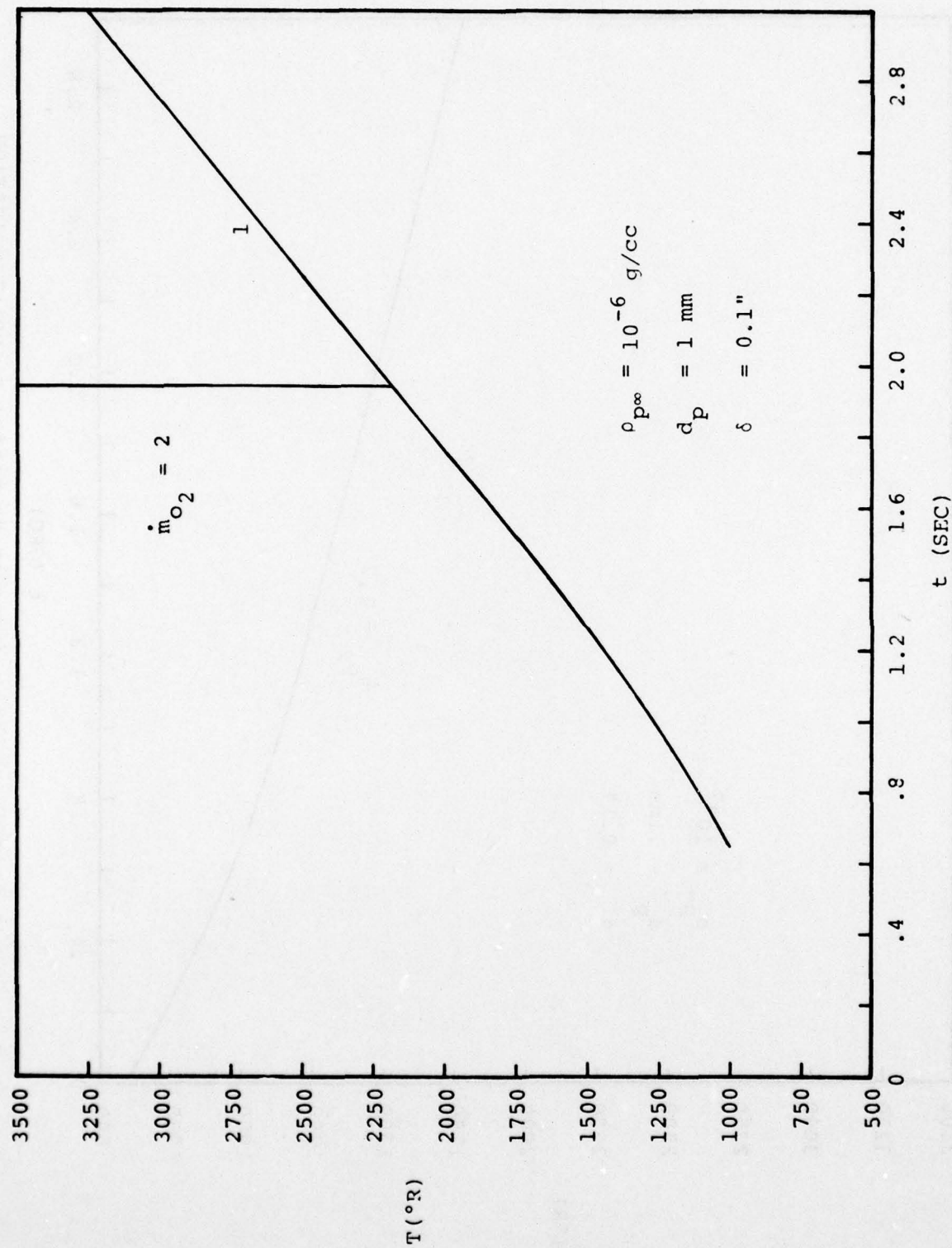


FIGURE 4-13c. TITANIUM RESPONSE TO PARTICLE IMPACT-OXIDATION

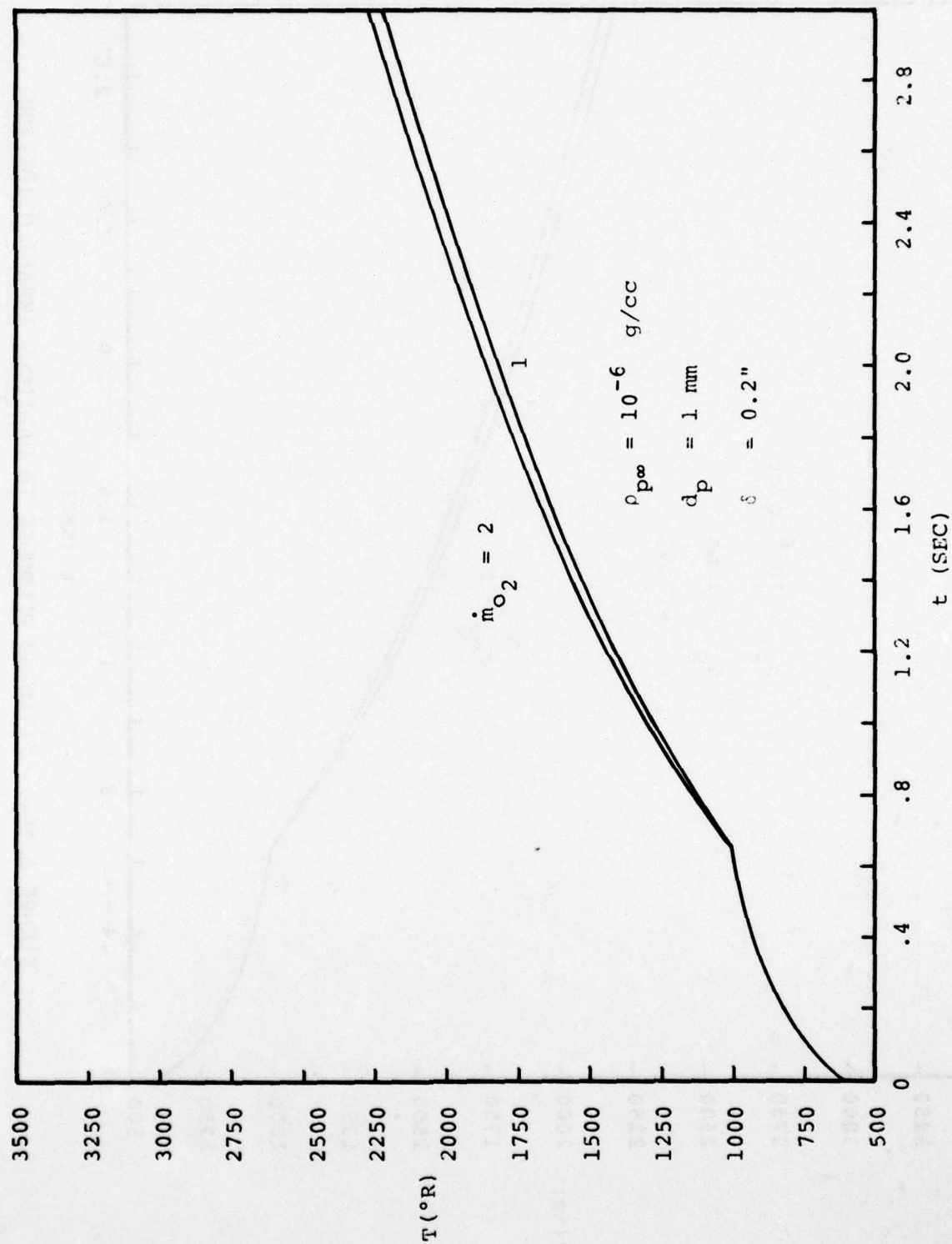


FIGURE 4-13D. TITANIUM RESPONSE TO PARTICLE IMPACT-OXIDATION



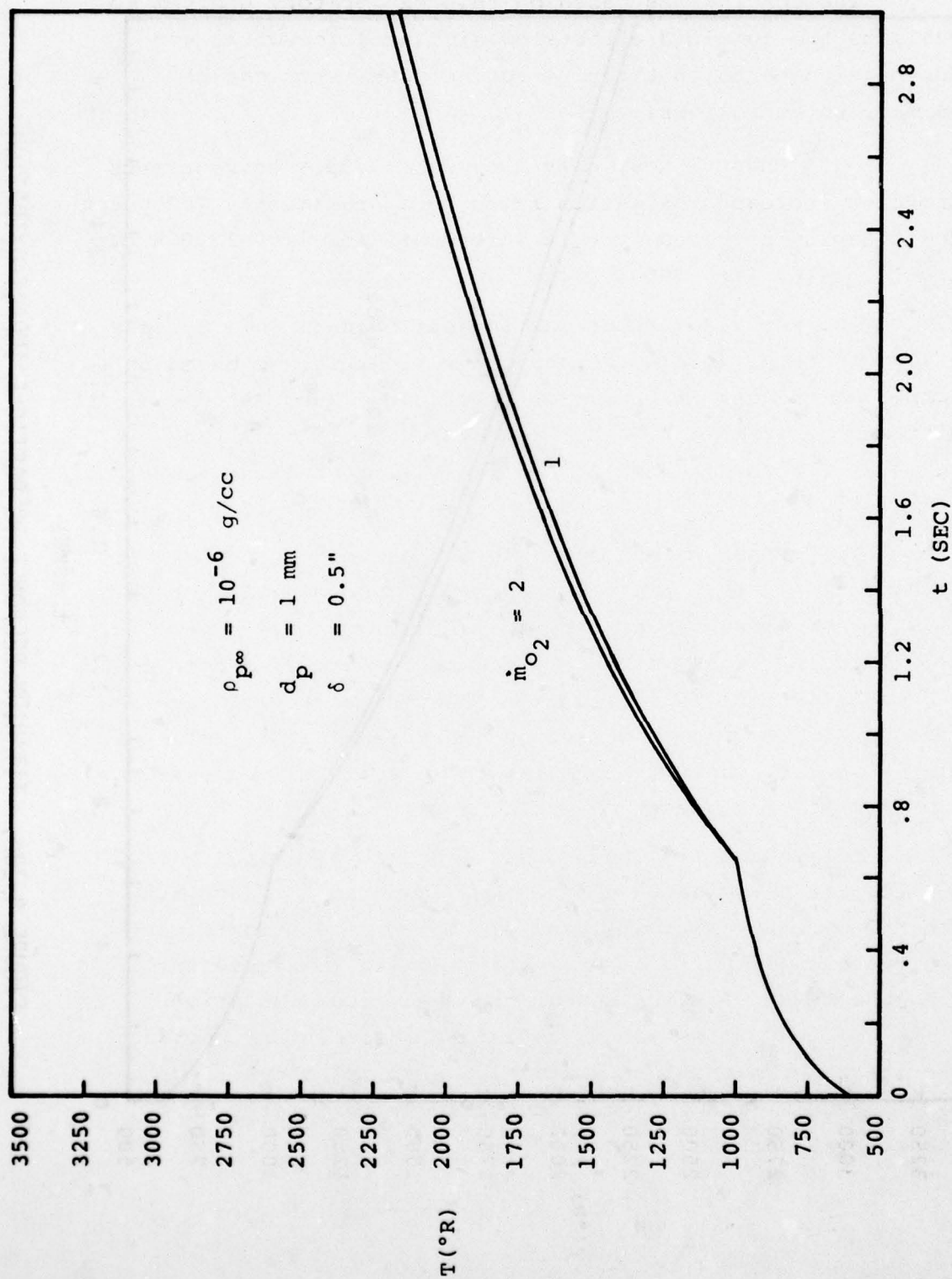


FIGURE 4-18E. TITANIUM RESPONSE TO PARTICLE IMPACT-OXIDATION

## 5.0 CONCLUSIONS AND RECOMMENDATIONS

The conclusions based on this exploratory program to evaluate the combined effects of simulated ice/water and dust environments on titanium surface chemistry can be summarized as follows:

(1) Phase I test data show water vapor environments produced increased oxidation rates by approximately 100 percent for titanium compared to  $O_2$  environments for 1200-1500°K but similar rates for 1700°K.

Analytical calculations suggest changes in  $H_2O$  vapor oxidation rates with temperature may be explained based on competing effects of diffusion coefficient (increased  $H_2$  diffusion coefficient with temperature in titanium) and solubility (decreased  $H_2$  solubility with increasing temperature).

(2) Phase I test data shows apparent pressure effect on oxidation rate. Analytical modeling where oxidation is solid-phase diffusion-controlled contradicts this experimental result. Assessment of literature data also contradicts this experimental result. The possibility of gas-phase rate-limiting processes in the Phase I test results may be an explanation. However, the overall evidence from the literature suggests no pressure effect.

(3) Phase II combined  $H_2O$  and dust data in the AEDC DET suggest a dominance of the heat absorbed in vaporizing the  $H_2O$  over any heat released due to surface oxidation. The overall effect is a net cooling due to the presence of condensed  $H_2O$ . Application of the analytical oxidation model to the DET test data shows good agreement predicting the on-set of significant oxidation heat release at approximately 2000°F with ignition occurring at temperatures in excess of 2500°F.

(4) Phase III tests comparing ice and glass single impacts on titanium in oxidizing environments showed no ignition for a bulk temperature of 1700°F ( $\sim$ 1200°K). The ice produced a smaller crater than the glass, but similar oxide coating spallation.

The overall conclusion from this exploratory program is that nuclear cloud ice/water will not significantly affect titanium oxidation response. Design criteria developed from extensive dust environment studies are still valid. No ignition is expected if titanium bulk temperatures remain below approximately 2000°F. Ignition can be expected above approximately 2500°F.



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